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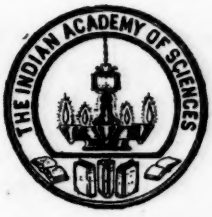

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SULPHUR DYES AND SULPHURISED VAT DYES

Part II. Constitution of Cibanone Yellow R—Part I

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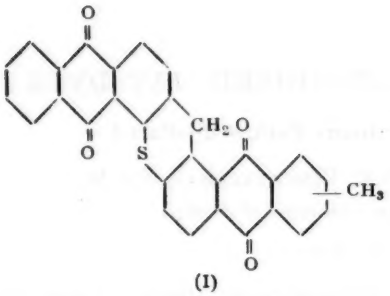
Received May 2, 1949

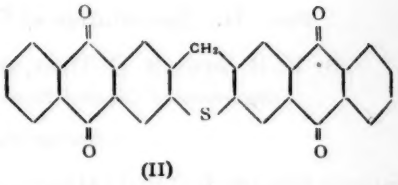
Cibanone Yellow R (Ciba) (Mayer and Schaarschmidt, 1908)[1] is a vat dye which dyes bright orange-yellow shades from a red-brown alkaline hydrosulphite vat. The dye is prepared by the fusion of 2-chloromethylanthraquinone with sulphur, followed by treatments with concentrated sulphuric acid and sodium hypochlorite. The shades are attractive and have moderate fastness to chlorine, but the dye has been withdrawn from the commercial range of Cibanone colours on account of its tendering action on cellulose when the dyed material is exposed to light. The catalytic activity in the photochemical degradation of cellulose is indeed so marked that it has been the dye of choice, together with Cibanone Orange R which is obtained by carrying out the thionation at a higher temperature, for investigators studying the accelerated oxidation of cellulose by the action of light and of oxidising agents.

The constitution of Cibanone Yellow R and Orange R has been examined by Fierz-David and Geering.[2] After removal of inorganic salts by means of hot water, the commercial dyes were extracted with alcohol, and from the extracts of both the dyes 2-methylanthraquinone was isolated. Purified Cibanone Yellow R analysed as follows:—C, 76·1; H, 3·4; S, 8·5. M. W. by Rast's method in perylene, 495. $C_{30}H_{16}O_4S$ requires C, 76·2; H, 3·4; S, 6·8%. M. W. 472. Chromic acid oxidation gave anthraquinone-2-carboxylic acid; but the dye was stable to hydrogen peroxide. From these results it was concluded that the dye was probably an anthraquinone-thioxanthene (diphthaloylthioxanthene) (I) or (II; with a methyl substituent). The linear compound (II) was synthesised by condensation of phthalic anhydride and thioxanthene in the presence of aluminium chloride, followed by cyclization. The product dyed much weaker shades than Cibanone Yellow R, to which the angular structure (I) was then assigned.

There are several considerations which render the constitution (I) very improbable. There is a considerable difference in the sulphur content between the theoretical and experimental values. Diaryl sulphides are

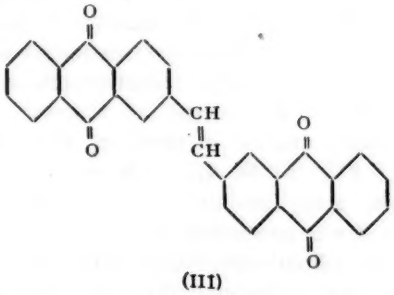


(I)



(II)

generally oxidised to sulphones and do not undergo fission by treatment with chromic acid in glacial acetic acid.[3] If, however, oxidation accompanied by desulphurisation does take place, (I) should give a mixture of anthraquinone-1-carboxylic acid and the 2-isomer, while only the latter acid has been isolated. The elementary analysis of the synthetic compound prepared by Fierz-David and Geering was also not in agreement with the theoretical value for (II), and the differentiation made by them between the angular (I) and the linear structure (II) on the basis of colour in concentrated sulphuric acid (I gives a blue and II a dark green colour) does not appear to be significant. Purified Cibanone Yellow R actually gives a characteristic purple and not a blue solution in sulphuric acid, and 2:2′-dianthraquinonylethylene (III) (Anthraflavone), which can be regarded as a linear *trans* compound, also gives a similar colouration.



(III)

The chemistry of Cibanone Yellow R and Orange R has now been reinvestigated, and it has been found that the purified Yellow R, assumed as homogeneous by Fierz-David and Geering, is a mixture of several substances. When a solution of the purified Yellow R in acetylene tetrachloride was chromatographed on alumina, three small bands developed on the column and were strongly adsorbed. The major part of the dye, which was unadsorbed, was recovered by concentration of the percolate and gave curved

orange needles, m.p. 368–70°, which we consider to be the essential tinctorial constituent of Cibanone Yellow R from the dyeing and other properties. The dye, m.p. 368–70°, was further recrystallized from acetylene tetrachloride, and subsequently from trichlorobenzene, but the m.p. and the elementary analysis remained unaltered. Concentration of the mother liquor after separation of the pure dye, m.p. 368–70°, gave a second crystalline component, m.p. 385–405°. The second component on further recrystallization from acetylene tetrachloride gave lemon yellow needles, m.p. 418–20°, which was not depressed by admixture with Anthraflavone (III) prepared according to Ullmann and Klingenberg.[4] One of the minor constituents of commercial Cibanone Yellow R is therefore Anthraflavone. A search was then made for further components. The commercial dye was purified by extraction with hot water, alcohol and nitrobenzene. The nitrobenzene extract was steam distilled and gave the more soluble components of the commercial dye which were distinguished from the pure dye and Anthraflavone by the olive-yellow solution the first gave in sulphuric acid as against the purple solution given by the pure dye and Anthraflavone. The more soluble components (m.p. 200–50°) contained sulphur, but they did not dye cotton, and we have not so far succeeded in further fractionating the mixture.

Elementary analysis of the pure dye (referred to hereafter as pure Cibanone Yellow R), m.p. 368–70°, corresponds to the empirical formula $C_{45}H_{26}O_7S$ indicating three methylanthraquinone residues to one atom of sulphur. In order to determine if the dye is a derivative of 2-methylanthraquinone obtained by sulphurisation through the alkyl group or if it possesses a structure such as (I), in which two anthraquinone residues are linked through a methylene group, desulphurisation of the pure dye by means of Raney nickel was undertaken. If the dye had the structure (I), removal of sulphur should lead to a dianthraquinonylmethane derivative, while if the dye was derived from 2-methyl-anthraquinone by sulphurisation through the alkyl group it should lead to a derivative of 2-methylanthraquinone, which could then be compared with the reduction product obtained from 2-methylanthraquinone.

Desulphurisation of the dye in boiling morpholine by means of Raney nickel gave a mixture of products from which a pale yellow crystalline sulphur-free compound (M. W. 250), m.p. 170°, was isolated after exhaustive purification; it was different from 2-methylanthraquinone as shown by the lower m.p. on admixture with the latter. Reduction of the dye in aqueous sodium hydroxide with Raney nickel gave a sulphur-free semi-solid product which was very difficult to purify. When a chloroform solution of this

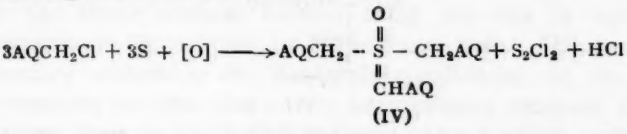
product was chromatographed through a column of alumina four fractions were isolated. The major fraction gave a product which after repeated crystallization gave pale yellow needles, m.p. 225–27° (M.W. 250) which analysed for $C_{15}H_{16}O_3$. The last fraction in the chromatographic separation gave a colourless crystalline substance which was similar to the crystalline reduction product obtained from 2-methylanthraquinone by treatment with Raney nickel under similar conditions.[5] When Anthraflavone was treated with Raney nickel in aqueous alkali, most of it was recovered unchanged, indicating the stability of the carbon-carbon linkage between the two anthraquinone molecules in Anthraflavone. It has likewise been observed by Diesbach and Quinza[6] that Anthraflavone was unaffected by catalytic reduction or by treatment with copper powder and hydrochloric acid, but was reduced to the corresponding dianthraquinonylethane by reduction with aluminium powder and hydrochloric or sulphuric acid. The M.W. of the major part of the reduction products from pure Cibanone Yellow R isolated in either of the reductive desulphurizations, the close similarity of the reduction products from the dye and 2-methylanthraquinone and the resistance of the ethylene linkage in Anthraflavone to fission by similar treatment with Raney nickel, indicate the absence of a dianthraquinonylmethane residue as in the constitution (I) proposed by Fierz-David and Geering. On the other hand, these observations offer strong support to a structure such as (IV) in which sulphurisation through the alkyl group in 2-methylanthraquinone is visualized.

Reductive degradation of pure Cibanone Yellow R by zinc dust, fused zinc chloride and sodium chloride,[7] at 430–40°, led to 2-methylanthracene, which was identified by direct comparison with an authentic specimen prepared from 2-methyl anthraquinone by a similar reduction. In addition to 2-methylanthracene a very small quantity of another sulphur-free degradation product was also isolated, which has not as yet been characterized. Treatment of Anthraflavone (III) under similar conditions also gave 2-methylanthracene and another degradation product which has not been identified. While the cleavage of the carbon-carbon linkage in Anthraflavone is understandable in view of its ethylenic character and the drastic pyrolytic treatment involved, it is doubtful whether the methylene bridge between the anthraquinone groups in dianthraquinonylmethane ($AQ - CH_2 - AQ$; AQ = 2-anthraquinonyl), which forms the essential feature in the constitution (I) proposed by Fierz-David and Geering, will break down even under such drastic treatment. The degradation of pure Cibanone Yellow R to 2-methylanthracene, therefore, gives further support to the conclusion that the dye is formed by the sulphurization of 2-methylanthraquinone through the methyl group. A study of the Clar degradation[7]

of dianthraquinonylmethanes and their derivatives, however, will be undertaken for comparison with the behaviour of pure Cibanone Yellow R and Anthraflavone.

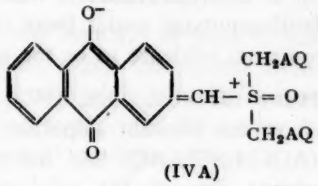
The hydrolysis of pure Cibanone Yellow R has not led to any definite conclusions as regards its constitution. The dye was stable to boiling alkaline hydrosulphite. The solution in carbitol gave a characteristic red-brown colour change on treatment with sodium hydroxide. It was stable to concentrated sulphuric acid at room temperature, to aqueous sodium hypochlorite (28 g. of available chlorine per litre) at 100° for one hour, and to boiling with copper bronze in nitrobenzene for 5 hours.

Taking into consideration the method of preparation of Cibanone Yellow R from 2-chloromethylanthraquinone, as well as its properties, it is suggested that the dye has the constitution (IV) and is probably formed by the following overall reaction.

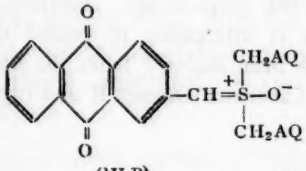


(IV)

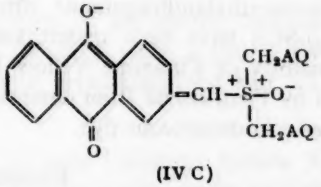
The intense colour of the dye and its stability are associated with resonance among structures such as (IV), (IV A), (IV B) and (IV C). The constitution (IV) is in agreement with the following facts: (1) Elementary analysis of



(IV A)



(IV B)



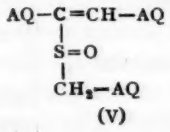
(IV C)

pure Cibanone Yellow R; (2) Oxidation of the dye to anthraquinone-2-carboxylic acid; and (3) Reductive desulphurization of the dye to derivatives of 2-methylanthraquinone and to 2-methylanthracene.

Considering the difficulties in the preparation of pure 2-chloromethylanthraquinone due to simultaneous production of 2-dichloromethylanthra-

quinone, it is conceivable that the starting material employed for the thionation may be either the dichloro derivative, which is more readily accessible, or the crude chlorination product, containing mono- and dichloro methylanthraquinones, instead of pure 2-chloromethylanthraquinone. When the dichloromethyl derivative was fused with sulphur at 280°, a brownish yellow dye, m.p. $> 500°$, was however obtained. Thionation of pure 2-chloromethylanthraquinone under similar conditions on the other hand, gave a mixture of two dyes, one of which was identical with pure Cibanone Yellow R; the other dyed orange-yellow shades and did not melt up to 500°.

In addition to the constitution (IV), alternative structures such as (V), derived from Anthraflavone (III) are also being considered for pure Cibanone Yellow R, in view of the following:—(1) the facile conversion of 2-methyl- and 2-dichloromethylanthraquinone to (III); (2) the conversion of *bis*-



(V)

2-anthraquinonylmethyl sulphide ($AQCH_2SCH_2AQ$) to (III); (3) the occurrence of (III) in the commercial dye; and (4) the possibility of an addition reaction between (III) and 2-mercaptomethylanthraquinone. However, since Anthraflavone is stable to catalytic reduction while the dye is degraded to derivatives of 2-methylanthraquinone under these conditions, the constitution (IV) appears on the present evidence to be the most probable.

Experiments to synthesise the compound (IV) and other analogous model structures starting from the relevant sulphides such as *bis*-2-anthraquinonylmethyl sulphide ($AQCH_2SCH_2AQ$) and halogeno derivatives such as 2-chloromethylanthraquinone through the sulphonium chlorides [*e.g.*, $(AQCH_2)_3SCl$] have been undertaken. It is interesting to record that a small quantity of Cibanone Yellow R has been isolated from the product obtained by Fierz-David from commercial Cibanone Orange R and regarded by him as a homogeneous dye.

Experimental

Purification of Cibanone Yellow R

(i) Commercial Cibanone Yellow R (8 g.) was purified by the exhaustive extraction method of Fierz-David; yield 1·85 g. A solution of the purified dye (0·25 g.), m.p. 358–60°, in acetylene tetrachloride (700 c.c.) was chromatographed through alumina when three small brown-coloured bands

developed. The unadsorbed dye was recovered from the acetylene tetrachloride percolate, and after concentration and cooling gave short, curved, orange needles, m.p. 368–70°. After recrystallization from the same solvent, the m.p. remained unaltered. (Found: C, 76·1; H, 3·6; S, 4·4. $C_{45}H_{26}O_7S$ requires C, 76·1; H, 3·7; S, 4·5%.) It was also observed that the elementary analysis of the dye crystallized twice from acetylene tetrachloride did not change after further recrytallization of the dye from trichlorobenzene.

The pure dye gave a uniform chromatogram when chromatographed in the oxidised state on alumina or in the reduced condition on filter-paper by the glass plate technique.[8] It is to be noted, however, that a mixture of pure Cibanone Yellow R, m.p. 368–70°, and Anthraflavone, m.p. 418–20° melted at 366–368°, and hence the constancy of m.p. in the purification of Cibanone Yellow R cannot be regarded as indicative of its homogeneity. Secondly, the above artificial mixture could also not be separated by chromatography in the oxidised or in the leuco state. The constancy of the elementary analysis in the further recrystallization of the pure dye however supports the view that it is a homogeneous chemical compound. The empirical formula $C_{45}H_{26}O_7S$ indicates three methyl anthraquinone residues to one atom of sulphur. The pure dye dyed a shade similar to the original dye and is regarded as the essential tinctorial constituent of the commercial dye.

The filtrate after the removal of pure Cibanone Yellow R was further concentrated and cooled, when the second component of the purified dye separated. This component after crystallization from acetylene tetrachloride gave lemon-yellow needles, m.p. 418–20°, alone or mixed with an authentic sample of Anthraflavone,[4] described later.

The mother liquor after the separation of the second component was diluted with excess of light petroleum (60–80°), when a yellow precipitate, m.p. 200–50°, separated. It could not be crystallized and had no affinity for cotton.

(ii) A quick method of isolation of pure Cibanone Yellow R was to extract commercial Cibanone Yellow R (25 g.) with water and then with carbon disulphide. The purified dye (15 g.) thus obtained was then extracted with boiling nitrobenzene (500 c.c.) when a moderately pure Cibanone Yellow R (10 g.), m.p. 368–76°, was obtained as residue. After further extraction with boiling acetylene tetrachloride to remove traces of Anthraflavone, it gave m.p. 368–72°.

Degradation of Cibanone Yellow R

Raney nickel reduction of Cibanone Yellow R.—(i) The dye (1 g.), Raney nickel (15 g.) and morpholine (50 c.c.) were heated under reflux for 12 hours with mechanical agitation and filtered. The filtrate was concentrated and then poured into hydrochloric acid, and the precipitate obtained (0·72 g.) was extracted with chloroform. The chloroform solution was chromatographed through alumina, and the chromatogram developed with the same solvent. Two brown fractions were strongly adsorbed; the percolate gave a sticky solid on removal of the solvent. It was dissolved in benzene and again passed through alumina. Two brown and a pink fraction were strongly adsorbed, and concentration of the percolate gave pale yellow needles, m.p. 170–172°, unaltered by further recrystallization from benzene-alcohol. (Found: C, 81·3; H, 7·3%. M.W. cryoscopic in camphor 250). The M.W. of the product indicates that it contains one anthraquinone residue, but the analysis could not be correlated with any definite structure. It was reducible by alkaline hydrosulphite and could be recovered back by air oxidation. When mixed with 2-methylanthraquinone, m.p. 172–73°, it gave m.p. 130–35°.

(ii) Cibanone Yellow R (3 g.), sodium hydroxide (3 g.), Raney nickel (30 g.) and water (200 c.c.) were boiled under reflux for 8 hours. The reaction mixture was then acidified and filtered. The nickel residue was extracted in a soxhlet with chloroform when a sticky yellow solid (2·13 g.) was obtained. It was redissolved in chloroform and then chromatographed through alumina, using benzene for developing and eluting the chromatogram. A major yellow band and two smaller bands developed. The major fraction after concentration and dilution with alcohol gave a yellow solid (0·6 g.), m.p. 140–210°. The product from the final fraction, giving a red solution in chloroform-benzene, was crystallized from benzene-light petroleum (40–60°) and gave colourless needles, m.p. 225–30°.

The major reduction product was dissolved in chloroform and rechromatographed as above. The pale yellow product, isolated from the major fraction, m.p. 195–205°, after two recrystallizations from alcohol-benzene, gave pale yellow needles, m.p. 225–27°. (Found: C, 74·6; H, 6·5. M.W. cryoscopic in camphor 250).

The second reduction product (m.p. 225–30°) when crystallized from benzene and light petroleum (60–80°) gave short needles, softening and shrinking above 232°, m.p. 235–40°; when admixed with the reduction product (which softens and shrinks above 237°, m.p. 242–46°) from 2-methylanthraquinone prepared under similar conditions of reduction, it

softened and shrank above 235° and melted at 240–46°, indicating the probable identity of the two reduction products.

(iii) Cibanone Yellow R (0·2 g.), Raney nickel (0·2 g.) and morpholine (100 c.c.) were shaken with hydrogen in a Parr hydrogenator at 40 lbs. per sq. inch at room temperature for 5 hours. The dye was unaffected under these conditions.

Raney nickel reduction of Anthraflavone

Anthraflavone was prepared according to Ullmann[4] by heating ω-dibromomethylanthraquinone with copper bronze in nitrobenzene. The product obtained after crystallization from nitrobenzene and subsequently from tetralin melted at 418–20°. Ullmann has stated that Anthraflavone does not melt up to 430°. (Found: C, 82·0; H, 4·0. $C_{30}H_{16}O_4$ requires C, 81·8; H, 3·6%.) This product was used in all the subsequent reactions and for mixed melting points.

Anthraflavone was submitted to the Raney nickel reduction treatment as in (ii) above. Most of the Anthraflavone was however recovered unchanged after the treatment.

Clar reduction[7] *of Cibanone Yellow R.*—The pure dye (0·5 g.), fused zinc chloride (2·5 g.), sodium chloride (0·5 g.) and zinc dust (2·0 g.) were powdered together and gradually heated to 430–40° and kept at this temperature for ten minutes. A cream coloured solid (0·1 g.) sublimed above 320°. The product was resublimed at 220–30°/0·1 m.m. when lustrous colourless flakes were obtained. On crystallization from benzene-alcohol it melted at 204–06°, alone or mixed with an authentic specimen of 2-methylanthracene (0·25 g.), m.p. 205–07°, obtained from 2-methylanthraquinone (0·5 g.) by a similar method.

The residue left after sublimation of the above product was boiled with dilute hydrochloric acid and filtered. The resulting product was sublimed at 450–60°/0·1 m.m., when a dull brick red solid (80 mg.), m.p. 240–60°, was obtained, which has not yet been characterised.

Clar Reduction of Anthraflavone.—Anthraflavone (0·5 g.) was reduced as above. The sublimed product (0·25 g.) on fractional sublimation at 210–20°/0·1 mm. gave a product which was identified as 2-methylanthracene by direct comparison with an authentic specimen. The residue after removal of 2-methylanthracene was further heated at 420–30°/0·1 mm., when a pale yellow substance sublimed. It was extracted with excess of hot benzene-chloroform (1 : 1) when a cream coloured residue was obtained which decomposes above 300°.

Chlorination of Cibanone Yellow R and Anthraflavone.—Cibanone Yellow R as well as Anthraflavone gave anthraquinone-2-carboxylic acid in poor yields on passing chlorine into their solution in boiling nitrobenzene for 5 hours. Other byeproducts formed in the reaction could not, however, be identified.

Thionation of 2-chloromethylanthraquinone.— 2-Chloromethylanthraquinone (1 g.), prepared according to Conant and Fieser,[9] and sulphur (1 g.) were heated under stirring for 3 hours at 290°. The product was powdered and extracted with carbon disulphide. The residue (0·75 g.) was boiled with acetylene tetrachloride (100 c.c.) and filtered while hot. The insoluble product (0·3 g.) did not melt up to 500° and dissolved in sulphuric acid with a purple colour. It was unaffected by treatment with sulphuric acid and sodium hypochlorite. The reaction product which crystallized from the acetylene tetrachloride solution melted at 364–72°, alone or mixed with pure Cibanone Yellow R and dyed the same shade as pure Cibanone Yellow R. The mother liquor after separation of the above crystalline product on dilution with light petroleum (60–80°) melted at 150–60° (decomp.).

Summary

The invalidity of the constitution (I), proposed by Fierz-David and Geering, for Cibanone Yellow R, a dye which is noted for its catalytic activity in the photochemical degradation of cellulose, is discussed. The purified dye, assumed to be homogeneous by Fierz-David, has been shown to be a mixture of several substances by chromatographic adsorption on alumina. The major tinctorial constituent crystallized from acetylene tetrachloride in curved needles, m.p. 368–70°. Anthraflavone was among the other products isolated.

Elementary analysis of pure Cibanone Yellow R is in agreement with the empirical formula $C_{45}H_{26}O_7S$, corresponding to three methylanthraquinone residues for one atom of sulphur. Reductive desulphurisation of the pure dye by treatment with Raney nickel and pyrolysis with zinc dust indicate that 2-methylanthraquinone residues are linked together through the methyl groups by means of sulphur, as against the methylene bridge between anthraquinone groups in the constitution (I) proposed by Fierz-David. The structure (IV) is suggested for pure Cibanone Yellow R.

Acknowledgment

We are indebted to the Council of Scientific and Industrial Research under whose auspices the work was carried out; to Mr. T. S. Gore for

the microanalyses recorded in the paper; and to Messrs. Imperial Chemical Industries (Dyestuffs Group) for gifts of chemicals.

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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XXI. Another Synthesis of Nobiletin

By V. V. Sreerama Murti and T. R. Seshadri

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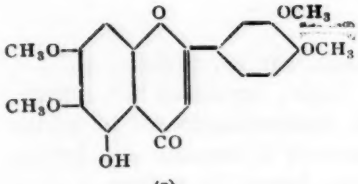
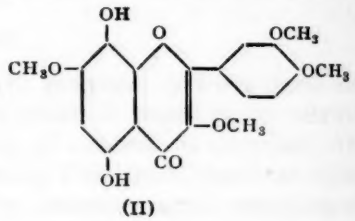
Received May 9, 1949

In Part XI[1] was reported a synthesis of nobiletin involving the *p*-oxidation of 5-hydroxy-6: 7: 3′: 4′- tetramethoxy flavone (I) using alkaline persulphate. More recently was explored successfully the alternative route of ortho-oxidation in the 6-position using as typical example the conversion of the gossypetin derivative (II) into 6: 8-dihydroxy quercetin.[2] The two stage process of ortho oxidation was used. This method has now been applied to the synthesis of nobiletin, the analogous member of the flavone group.



(I)



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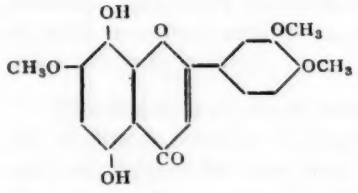
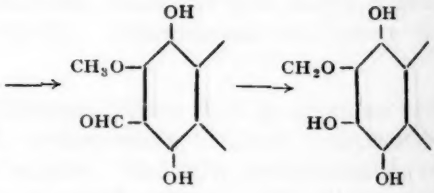
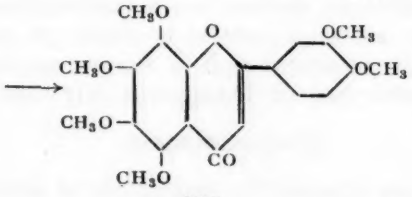


(III)



(IV) (V)



(VI)

5: 8-Dihydroxy-7: 3′: 4′ trimethoxy flavone (III) required for this purpose was recently described by Rao, Seshadri and Viswanadham.[3] Its condensation with hexamine takes place satisfactorily yielding the corresponding 6-aldehyde (IV). Subsequent oxidation with hydrogen peroxide also proceeds well, the resulting compound (V) being a useful partial methyl ether of non-nobiletin. Further methylation yields nobiletin (VI) which is identical with samples obtained by earlier methods.

Experimental

5: 8-Dihydroxy-7: 3′: 4′-trimethoxy flavone-6-aldehyde (IV)

5: 8-Dihydroxy-7: 3′: 4′-trimethoxy flavone (III) was prepared according to the method of Rao, Seshadri and Viswanadham.[3] It (2 g.) was dissolved in glacial acetic acid (25 c.c.) and hexamine (6 g.) was added to the yellow solution. The mixture was gently refluxed for 6 hours, a mixture (10 c.c.) of equal volumes of fuming hydrochloric acid and water added and refluxing continued for another 15 minutes. The dark red solution was the diluted, saturated with sodium chloride and the aldehyde extracted with a large volume of ether. On distilling off the ether, a yellow solid was obtained which crystallised from alcohol-acetic acid mixture as yellow prisms melting at 262–4°; yield, 0·6 g. The compound dissolved in aqueous sodium hydroxide with a yellow colour and gave a brown-red colour with ferric chloride in alcoholic solution. (Found: C, 61·6; H, 4·4; $C_{19}H_{16}O_8$ requires C, 61·3; and H, 4·3%). The dinitrophenyl hydrazone was prepared and was found to melt at 253–5°.

5: 6: 8-Trihydroxy-7: 3′: 4′-trimethoxy flavone (*V*)

The above aldehyde (1 g.) was dissolved in a mixture of 2 N sodium hydroxide (6 c.c.) and pyridine (5 c.c.) and the yellow solution was treated with 6% hydrogen peroxide (4 c.c.) in small quantities while cooling in ice-water. The mixture was occasionally shaken during half-an-hour, then acidified with dilute hydrochloric acid, and extracted with ether. The solid left behind after removing the solvent was crystallised from rectified spirit when it was obtained as bright yellow rectangular rods melting at 271–2°; yield, 0·5 g. It gave a deep reddish brown colour with alcoholic ferric chloride. (Found: C, 60·2; H, 4·6; $C_{18}H_{16}O_8$ requires C, 60·0; and H, 4·4%).

Nobiletin

The trihydroxy compound was completely methylated in acetone solution using excess of dimethyl sulphate in the presence of anhydrous potassium carbonate. The product crystallised from methyl alcohol as pale yellow

needles melting at 132–3° and was identical in all respects with a sample of nobiletin prepared earlier.[1]

A correction

In the earlier paper,[1] the melting point of 5: 6: 7: 3′: 4′-pentamethoxy flavone was reported as 142–43° and the sample was considered to contain half a molecule of water of crystallisation. Subsequently it has been found that in this case there was an error owing to the incomplete deacylation in the 3-position of the Allan-Robinson condensation product when boiling for half an hour with 5% aqueous sodium carbonate was used. Boiling for two hours seems to be necessary. Using this modification the pentamethyl ether is found to crystallise from alcohol as colourless needles melting at 172–3°. (Found: C, 64·7; H, 5·7; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·4%.)

Summary

A new synthesis of nobilein has been achieved employing the two stage process of ortho-oxidation. 5: 8-Dihydroxy-7: 3′: 4′-trimethoxy flavone (III) is condensed with hexamine to yield the 6-aldehyde (IV) which undergoes smooth oxidation with hydrogen peroxide to 7: 3′: 4′-trimethyl ether (V) of nornobiletin. Final methylation of (V) produces nobiletin (VI).

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CHEMICAL INVESTIGATION OF INDIAN LICHENS

Part VIII. Some lichens growing on sandal trees (*Ramalina tayloriana* and *Roccella montagnei*)

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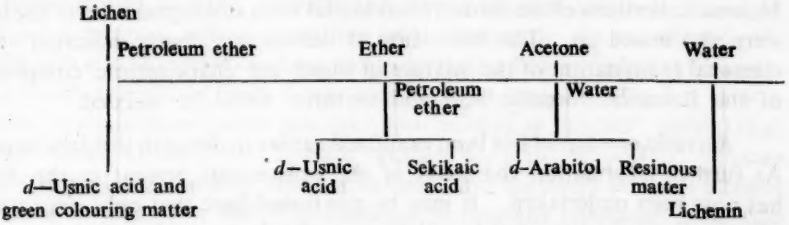
It was reported to us recently that sandal trees grown on the Simhachalam hills which are in the neighbourhood of Waltair have been suffering from the adverse effects of the growth of lichens on them. The tender growing parts of the plants have a heavy growth of lichens and these parts soon deteriorate and die. A sample of the predominant lichen was sent to Kew for identification and it has been identified as *Ramalina tayloriana* Zahlbr. (*Ramalina canaliculata* Tayl. non-diet.). A chemical examination of the components using the general procedure adopted in the previous papers of this series has established the presence of *d*-usnic acid, sekikaic acid and *d*-arabitol. Two methods of extraction have been adopted using the sequence of solvents, petroleum ether, ether, acetone and water in the first instance and omitting petroleum ether in the second owing to lack of this solvent. Usnic acid is quite soluble in petroleum ether especially in the presence of green colouring matter and rather sparingly in ether, whereas sekikaic acid is insoluble in the former and freely soluble in the latter. Consequently usnic acid was obtained mostly from the petroleum ether extract and to a small extent from the ether extract while sekikaic acid was found only in the ether extract. The subsequent acetone extract yielded *d*-arabitol. In the second set of experiments in which petroleum ether was omitted usnic acid was obtained both from ether and acetone fractions.



In the nature of its chemical components *R. tayloriana* resembles closely *R. geniculata*[1]. Among the large number of species of the Ramalinæ so far

examined usnic acid seems to be almost invariably present; sekikaic acid which is said to be found only in the Ramalinæ[2] has been reported previously to be present in *R. dilacerata*[3], a Chinese drug known as ' Shi-hoa', *R. farinacea*[1] and *R. geniculata*[1]. Similarly *d*-arabitol[4] has been previously noted to occur in *R. scopularum* and *R. geniculata.*

In considering the possible cause of injury to the sandal trees may be mentioned here the statement of Porter[5] that the Ramalinæ are capable of causing damage to the tissues of trees by their penetrating bases. In the present case the lichen was actually found to have penetrated deep into the tissues of the sandal trees; more markedly the tender parts were attacked. This feature was also observed in other plants growing nearby and they were also adversely affected. Besides the physical injury mentioned above, it appeared to us possible that certain lichen products may have a phytocidal effect which may require consideration. Hence some experiments on the toxic properties of the components of this lichen have now been made using fish as test-animals. Usnic and sekikaic acids are found to be markedly toxic to fish and consequently some phytocidal action could be expected from them. Previously vulpinic and pinastric acids were noted to have toxic effect on living animals[6]. Usnic and sekikaic acids may now be added as poisonous lichen components. From the tentative constitution given to the former it contains the toxophore (A) and the latter has in it the grouping (B) (see Lauger *et al.*[7] and Seshadri *et al.*[8]). Here may also be mentioned the recent discovery of Stoll *et al.*[9] that usnic acid inhibits the growth of Staphylococcus aureus and various mycobacteria, but is inactive against Gram-negative bacteria.

(A) (B)

Ramalina tayloriana is found mostly at higher altitudes of the range above 1000 ft. whereas *Roccella montagnei* is more common at the lower altitudes. In some collections of the former from sandal trees small quantities of the latter were also mixed up. This admixture of lichens was clearly indicated by the chemical examination of the mixture in which the characteristic components of the Roccella, roccellic acid and erythrin, could be isolated.

Roccella montagnei has been examined earlier in detail in this laboratory[10]. As further information the study of the carotenoids present in this lichen has now been undertaken. It may be mentioned here that only stray studies of vitamin properties of lichens[11] have so far been made. Only traces of vitamin D and some ergosterol were noticed in *Cladonia rangiferina.* Short growth lichens of Alaska gave some vitamin A when fed to rats.

The presence of vitamin C was also detected by acetic acid-silver nitrate reagent. No study of the carotenoid pigments of lichens seems to have been carried out so far. We expected that lichens belonging to the foliose type (leafy and green) might contain high percentage of carotenoids just like green leaves. Further in view of (1) the contribution of algæ and fungi to the discovery of new carotenoids, (2) the presence of both these in lichens and (3) the fodder value of lichens, there appeared to be considerable interest in this particular study. Fairly high percentage of β-carotene and small amounts of kryptoxanthin are found to be present in *Roccella montagnei*. The part played by climatic conditions is also revealed in the difference between samples obtained from Waltair and from Nagarcoil in South Travancore which is located nearer to the Equator and is warmer and more humid with a higher rainfall. Samples obtained from the latter contained about 40 mg. of β-carotene per hundred grams of air-dry lichen whereas the Waltair sample contained less, about 28 mg./100 g. and both of them compare very favourably with other natural sources of β-carotene.

In the experimental portion not only is the estimation of the carotenoids described but also an improved method of separating the various components present. This lichen does not seem to exert any unfavourable effect on sandal trees probably because it does not penetrate the tissues of the plant and further has no toxic components as revealed by fish tests. It is, however, of interest in connection with the study of antibiotics. Roccellic acid derivatives have been found to be anti-tubercular[12] and more recently *l*-protolichesterinic acid and related lactone aliphatic acids have been discovered to have antibacterial proprties[13].

Experimental

Ramalina tayloriana

Extraction I.—Petroleum ether extract (d-*Usnic acid*).—The air-dried lichen (500 g.) was extracted with petroleum ether (b.p. 60-80°) in the cold by repeated maceration (three times, each time lasting for 24 hours). The solvent was then distilled and the concentrated extract allowed to stand over-night when some greenish yellow crystalline solid separated. It was filtered off, washed with a little petroleum ether and recrystallised twice from dry benzene. When finally crystallised from a mixture of chloroform and alcohol it was obtained in the form of yellow prismatic rods melting at 202-203°; yield, 1·8 g. (Found: C, 62·6; H, 5·0; $C_{18}H_{16}O_7$ requires C, 62.8; H, 4·7%). It was easily soluble in chloroform and hot benzene and sparingly in cold alcohol $[\alpha]^{30}$ in chloroform, + 469°. It dissolved in aqueous potassium hydroxide giving a yellow solution and in alcoholic solution it gave a reddish-brown colour with ferric chloride. It did not give any colour with bleaching

powder and did not undergo fission by treatment with dilute alkali (5%) like the depsides. With concentrated sulphuric acid it gave a deep yellow solution which turned orange-red on standing or addition of a drop of water. In view of all these properties the compound was identified as *d*-usnic acid. This was confirmed by preparing its acetate melting at 198-199° using acetic anhydride and pyridine.

Ether extract (*Sekikaic acid*).—The material left after extraction with petroleum ether was repeatedly extracted with ether in the cold till the last extract was almost colourless. The total extract was concentrated to a small bulk (concentration being effected in vacuo towards the end) and left over-night when a pale yellow solid separated out. It was filtered off, washed repeatedly with a good quantity of petroleum ether to remove any usnic acid and the colourless solid product crystallised from benzene when it was obtained in the form of colourless rectangular rods melting at 144°; yield, 4·5 g. (Found: C, 63·4; H, 6·3; $C_{22}H_{26}O_8$ requires C, 63·2; H, 6·2%.) It was insoluble in petroleum ether and easily soluble in alcohol and acetone. It was soluble in sodium bicarbonate solution and in alcoholic solution it was acidic to litmus and gave a violet colour with a drop of ferric chloride. It did not give any colour with bleaching powder. On acetylation with acetic anhydride and fused sodium acetate it gave a crystalline acetate melting at 162-163° (diacetyl sekikaic acid m.p. 162-163°). Therefore it was identified as sekikaic acid. This was confirmed by identifying its fission products as divaricatinic acid, m.p. 148° and hydroxy-divaricatinic acid, m.p. 157°.

Acetone extract (d-*Arabitol*).—The residue left after ether extraction was extracted with hot acetone (three times, each time lasting for 6 hours) and the combined extract after concentration was obtained as a sticky mass. It was divided into two fractions by treatment with water. The water-insoluble fraction consisting of a sticky reddish-brown resinous mass was removed by filtration and the clear aqueous solution concentrated on a water-bath. The viscous semisolid residue was left in a vacuum desiccator for some days when it gradually solidified to a sticky mass which could be obtained as a granular solid after washing with a large quantity of ether. It was very hygroscopic and when crystallised from a mixture of alcohol and acetone came out as colourless crystalline aggregates melting at 102-103°; yield, 0·5 g. It was sweet to taste and easily soluble in water, sparingly in alcohol and acetone and insoluble in ether. It gave no colour with ferric chloride and did not reduce Fehling's solution. On acetylation it gave a crystalline acetate melting at 73-74°. From these reactions it was identified as *d*-arabitol.

Water extract (*Lichenin*).—The residual lichen powder was finally boiled with water for 48 hours and the aqueous extract concentrated on a water-bath

when a brittle brown mass was obtained; yield, 15 g. It was insoluble in alcohol, sparingly soluble in cold water and easily soluble in hot water. It gave no colour with iodine or ferric chloride. It was quite soluble in ammoniacal copper sulphate solution. On hydrolysis with dilute hydrochloric acid it reduced Fehling's solution. It was therefore identified as lichenin.

Extraction II.—The lichen powder was first extracted with ether by cold percolation and then with hot acetone. The ether extract was concentrated to a small bulk and cooled when usnic acid separated out first as the less soluble component. The mother liquor was concentrated to a syrupy consistency and by judicious addition of petroleum ether sekikaic acid was precipitated and purified by crystallisation. The acetone extract was divided into two portions as before. A small quantity of usnic acid was obtained from the water-insoluble portion by treatment with ether, and *d*-arabitol from the water-soluble portion.

Mixed sample: Ramalina tayloriana + Roccella montagnei (*Usnic acid, Sekikaic acid, Roccellic acid and Erythrin*)

The powdered sample (50 grams) was extracted with petroleum ether, ether and hot acetone successively. From the petroleum ether extract *d*-usnic acid was obtained. The ether extract on concentration yielded a less soluble fraction consisting of a small quantity of *d*-usnic and mostly roccellic acids. The latter could be obtained pure by treatment with dilute sodium bicarbonate solution and subsequent acidification with dilute hydrochloric acid. When crystallised from acetone it was obtained as colourless rectangular rods melting at 132-33°. Mixed melting point with an authentic sample of roccellic acid was not depressed. From the original ether mother liquor by evaporation and treatment with a little pure chloroform, a small quantity of rocellic acid was left behind. The chloroform solution yielded sekikaic acid when treated with excess of petroleum ether.

The acetone extract on concentration to a very small bulk deposited a solid which when washed with cold water and crystallised from a mixture of alchohol and acetone came out as colourless needles melting at 154-55°. Mixed melting point with an authentic sample of erythrin was not depressed.

Roccella montagnei.—Two representative extractions were done, one with a sample obtained from Nagarcoil, South Travancore and the other with the sample collected in Waltair.

Ether extract.—The lichen in coarse powder form (300 g.) was repeatedly extracted with ether in the cold till the last extract was almost colourless.

The total extract was distilled to remove the solvent (reduced pressure was used for the last stages) and the semisolid residue was digested with petroleum ether (b.p. 40-60°, litre) and filtered (residue R). The filtrate was concentrated under reduced pressure to one-fifth of its volume and dried over anhydrous sodium sulphate. This solution was passed through a column of anhydrous alumina for chromatographic analysis. The lower-most region, broad orange red band, was eluted from the column itself by passing fresh quantities of the same solvent. This eluate was concentrated to a very small bulk and allowed to stand over-night when a beautiful crystalline solid in the form of lustrous violet-red plates separated. This was filtered off and recrystallised from benzene-methanol mixture when it was obtained as dark violet prisms in the form characteristic of β-carotene[14]; yield, 90 mg. from the Nagarcoil sample and 70 mg. from the Waltair sample. It melted at 183-184° and was optically inactive. It gave a deep blue colour with conc. sulphuric acid and a greenish blue colour with antimony trichloride in chloroform solution. Its identity as β-carotene was confirmed by its absorption spectrum in carbon disulphide solution, the absorption region being 520-485 mμ. Colorimetric estimation of the total pigment present in the eluted solution was carried out using a standard curve relating the Lovibond yellow units with pure β-carotene in micrograms per c.c. The value was 120 mg. in the case of the Nagarcoil sample and 85 mg. in the case of the Waltair sample. The other bands in the developed chromatogram were cut out and separately eluted with petroleum-ether containing ethanol (2%). The two upper most bands, olive green and bluish green were found to be due to chlorophylls and the next (lower one) orange yellow region was identified as kryptoxanthin by means of its absorption spectrum at the region 485-450 mμ (in petroleum ether b.p. 60-80°) and phase separation with methanol (95%) from petroleum ether solution. Colorimetric estimation was 2·5 mg. in the case of the Nagarcoil sample and 1·5 mg. in the case of the Waltair sample. In between the β-carotene and kryptoxanthin bands two very narrow reddish orange bands were observed which could not be identified.

The residue R was worked up according to the earlier method[10] and was found to consist of roccellic acid m.p. 133° (yield, 1·7% in Nagarcoil sample and 2·3% in Waltair sample), a small quantity of erythrin m.p. 155-56° and orcinol (yield, 0·2 and 0·6%).

Acetone extract.—The hot acetone extract was concentrated to the minimum bulk and ether was added in an equal amount when a colourless solid (1·0% in Nagarcoil sample and 1·2% in Waltair sample) was precipitated. This was filtered off, washed with ether and crystallised from alcohol when it came out as large hexagonal crystals melting at 122°. It was identified

as erythritol by preparing its acetate m.p. 91° and benzoate m.p. 185-86°. The acetone ether filtrate was evaporated off and treated with water. The water-insoluble portion was crystallised from acetone when erythrin (1·3 and 1·0%) was obtained. The aqueous filtrate was extracted three times with an equal volume of ether when orcinol was removed in the ether layer leaving montagnetol behind in water. The layers were separated and evaporated; orcinol (a small quantity) was obtained from the former and *r*-montagnetol (1·2% and 1·5%) m.p. 156° from the latter. This procedure facilitates easy isolation of montagnetol as compared with the earlier method.[15]

Toxicity tests.—Fresh water fish (*Haplochilus panchax*) were employed as experimental animals for the test which was carried out according to the method of Krishnaswami and Seshadri,[16] the 'turning time' being used as a measure of toxicity.

d-*Usnic acid.*—50 mg. of usnic acid was dissolved in 10 c.c. of hot absolute alcohol and the solution was poured into a litre of tap-water in a thin stream with continuous stirring. The average turning time for fish was found to be thirteen minutes. None of the fish recovered even after removal to fresh water and all died after some time.

Sekikaic acid.—The experiment was repeated using sekikaic acid instead of usnic acid and adding gelatin (one gram per litre of water) in order to increase the solubility of the compound in water. In a concentration of 100 mg. per litre the average turning time was found to be twenty-seven minutes and with 200 mg. the time taken was only 6 minutes. In both cases all the fish died without recovery. A peculiar slate-blue colour developed on the ventral side of the fish.

Summary

Ramalina tayloriana, a lichen growing on sandal-wood trees is considered to produce adverse effect on the trees both by physical injury caused by the hold fasts and by means of its toxic components, usnic and sekikaic acids which are found to be toxic to fish. *Roccella montagnei* appears to have no such effect. It is found to be rich in β-carotene. Convenient methods of separating the various components of these lichens are described.

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CHARACTERISTIC FREQUENCY AND CHEMICAL REACTIVITY

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Chemical reactivity as studied in rate measurements often involves only changes in one part of the molecule and the influence of a substituent in another part of the molecule on these changes. The reactions involve the rupture of some bonds and the formation of new ones. In a large majority of cases, these changes require an activation energy which is mostly computed from experimentally determined values of rate constants at different temperatures, using the well-known Arrhenius equation. Systematic changes in the molecule by introduction of substituents at specified parts of a molecule has shown that there is a corresponding variation in the activation energies. From *a priori* considerations, it may be expected that activation energies should be closely related to the bond stretching force constant of the bond primarily affected. Fugassi and Warrick[3] studied an empirical correlation in the case of some unimolecular reactions, while more recently, Flett studied a few reactions to correlate the rate constant with the characteristic frequencies.[2] With the polyatomic systems usually used in these investigations, it is not readily feasible to calculate the force constants; but, for purpose of comparisons, instead of using the frequency as such, the square of the frequency expressed in wave numbers may be expected to give a better picture because of its close relationship with the force constant of the bonds in question. In some cases, results are available only at a single temperature and a comparison of activation energies is clearly ruled out. In such cases, the logarithmic form of the Arrhenius equation suggests the use of the logarithms of rate constant, provided one can assume that the frequency factor remains the same. In the case of substituted benzene derivatives, the difference for a given series is small enough to use this assumption as a first approximation.

In the course of an analysis of the reaction between ethylene derivatives and bromine[1] it was noticed that there was strictly linear relation between the activation energy and the square of the characteristic frequency, provided the mechanism of the reaction was the same. In the present communication, a few other reactions are similarly analysed and the results are presented in Tables I and II and Figs. 1 and 2. The observations of Fugassi and Warrick as well as those of Flett are also considered in the sequel.

TABLE I*

Esterification and Hydrolysis of Esters

Substituent	Esterification			Acid hydrolysis	Alkaline hydrolysis
	log k	$\bar{\nu}^2_{c=0}\times10^{-6}$	$\bar{\nu}^2_{OH}\times10^{-7}$	E k. Calories	E k. Calories
p-Nitro ..		2·958	1·254	14·50	12·40
p-Iodo ..				16·70	
p-Bromo ..	1·0899	2·924		16·80	
p-Chloro ..	1·0569	2·934	1·260	16·80	
H- ..	1·2833	2·906	1·260	17·70	14·56
p-Methyl ..	1·2945	2·889	1·264	18·20	15·16
p-Methoxy ..		2·874	1·267	19·65	
p-Amino ..		2·856		20·00	16·70

* Activation energies from Moelwyn Hughes, *Reaction in Solution* (2nd edn. O. U. P.)

TABLE II

Reaction between Primary Amines and Acyl Halides

Substituent	Substitution in Amine			Substitution in Acyl halide	
	k_{NH}	$\bar{\nu}^2_{NH}\times10^{-7}$	E	$\bar{\nu}^2_{C=0}\times10^{-7}$	E
p-Nitro ..	6·729	1·181	11·80	3·186	5·90
p-Chloro ..	6·623	1·166	7·60	3·165	7·00
H ..	6·591	1·162	7·35	3·161	7·35
p-Methyl ..	6·577	1·159	6·80	3·154	7·80
p-Methoxy ..	6·541			3·150	

TABLE III

Reaction between Methyl Halides and Thiosulphate Ion

Halide	$\bar{\nu}^2_{C-X}\times10^{-4}$	E
Methyl Chloride ..	50·41	20·49
Methyl Bromide ..	36·00	19·23
Methyl Iodide ..	28·01	18·78

In every one of the instances chosen, a linear relation between activation energy and $\bar{\nu}^2$ is observed. Expressing activation energy in calories and the characteristic frequency in wave numbers, the curves obtained can be represented by an equation for a straight line of the form

$$E = a\bar{\nu}^2 + c,$$

where a and c are constants for a particular reaction. It will be observed that distinct differences are noticeable both in the magnitude and the direction of the slope of these lines.

The correlation between the characteristic frequency of the bond and the activation energy of the reaction is thus clear, and in all the cases this factor may be expected to contribute a large part of the observed activation

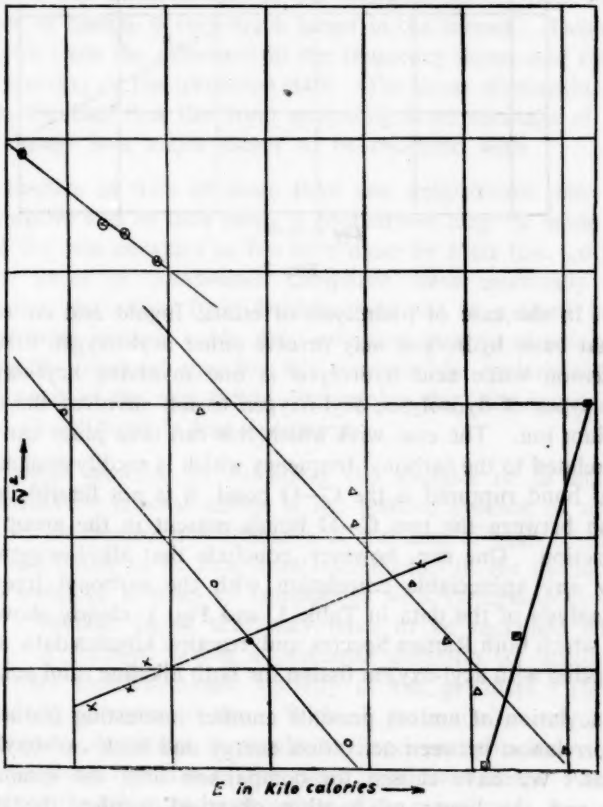

FIG. 1

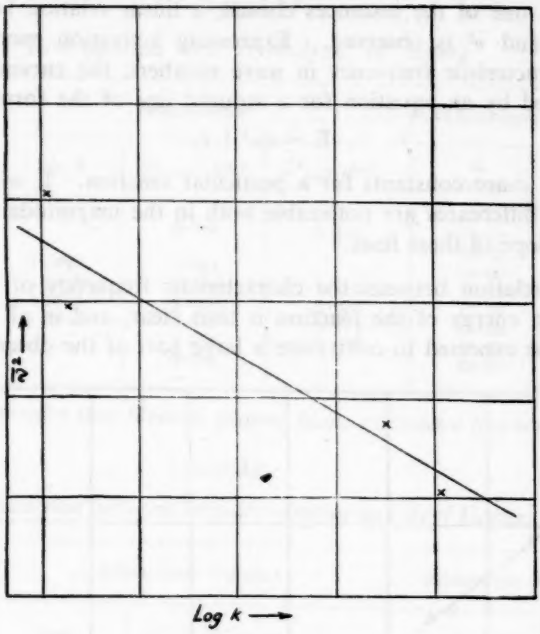

FIG. 2

energies. In the case of hydrolysis of esters, Ingold and co-workers[6] have shown that basic hydrolysis may involve either acyl-oxygen fission or alkyl-oxygen fission while acid hydrolysis is one involving acyl-oxygen fission. For both types of hydrolysis, acyl-oxygen fission involves the formation of a carbonium ion. The ease with which this can take place can be expected to be correlated to the carbonyl frequency which is readily assigned. Though the actual bond ruptured is the C—O bond, it is not feasible at present to distinguish between the two C—O bonds present in the group taking part in the reaction. One can, however, conclude that alkyl-oxygen fission will not show any appreciable correlation with the carbonyl frequency. The present analysis of the data in Table I and Fig. 1 clearly show that in the esters for which both Raman Spectra and reaction kinetics data are available, we are dealing with acyl-oxygen fission for both alkaline and acid hydrolysis.

The acylation of amines presents another interesting feature. There is a clear correlation between activation energy and both carbonyl and N—H frequencies. We have chosen for comparison only the symmetric N—H vibration and the linear relationship observed justifies the choice. The

transition state should involve both the N—H and the C—Hal. bonds but in the absence of a clear assignment of the C—Hal. bond in the compounds in question, we are forced to the next best alternative, namely, the carbonyl frequency. As in the case of ester hydrolysis, changes in the polarisability of the adjacent bond may be expected to correspond with changes in the carbonyl frequency with a possible reversal of sign. This expectation is substantiated by the slopes in Fig. 1. A negative slope is obtained when the carbonyl frequency is used for comparison while the N—H frequency gives a positive slope. This is only to be expected since the amino group is directly involved in the transition state.

The reaction between thiosulphate ion and methyl halides brings out another aspect of the problem. While the direction of the change in activation energy is the same as that of the characteristic C—Hal. frequency, the magnitude of change is very much larger in the former. This difference must arise both from the difference in the frequency factor and from differences in the stability of the transition state. The linear relationship indicates none the less the fact that the bond stretching force constant of the bond undergoing change is a major factor to be reckoned with.

In the absence of data at more than one temperature, rate constants alone are available and in such cases, a comparison may be made using the logarithm of the rate constant as has been done by Flett (*loc. cit.*) (Fig. 2). Provided the series of compounds compared have essentially the same frequency factor, deviations from linearity may not be noticed and in the case of substituted benzoic acids, this condition is approximately fulfilled. It can be readily observed that for this reaction, the polarisability of the acyl-oxygen bond is the one factor determining the rate-determining step and that the O—H bond is less significant.

The principal obstacle in extending the analysis or in making any rigorous quantitative generalisations is the relative absence of unequivocal assignments of characteristic frequencies in the case of such of those reactions which are found to be free from complexities in the mechanism in a homologous series or a series of compounds with systematic variations of substituents. Another factor that may have to be reckoned with is the probability of a reaction taking a preferred direction on account of the relatively greater thermodynamic stability of the products. The nitrogen halides are clear examples of this. With all these limitations, however, a certain amount of empirical extrapolations and interpolations are feasible in any one specified reaction of the types considered here. For instance, using the data in the tables and making use of the equation 1, one can predict

the activation energy for the alkaline hydrolysis of the halogeno and methoxy benzoic esters.

Mention was made earlier in this memoir that a close correlation between characteristic frequency and activation energy can be expected provided there is no mechanistic changes. The aliphatic substitution reactions thoroughly investigated by Hughes, Ingold and co-workers may be expected to provide us with a suitable material to test this but the frequency assignments in the case of the several compounds are not sufficiently accurate for proper comparison. One can reasonably expect that the grouping of frequencies will be on the same lines as the grouping of the compounds on a mechanistic basis by these workers.

It is of some interest to consider two instances where Fugassi and Warrick find considerable differences between their calculated values activation energies and the observed ones, the dissociation of nitrogen tetroxide and the decomposition of tertiary butyl alcohol. In the former case it is significant that the use of the experimentally determined value of the heat of the reaction makes the " calculated " value agree closely with the " observed " value. The discrepancy has to be attributed to several causes: the characteristic frequency assumed for the calculation appears to be surprisingly low. Analogy with the bonds involving carbon suggests that this should be in the neighbourhood of 1000 $cm.^{-1}$ instead of 283 mentioned. The monomer is stabilised by resonance involving structures with a three electron bond. This resonance energy may result in a lowering of the activation energy by its contribution to the transition state. Further, the adjacent charge rule of Pauling[8] which appears to be clearly substantiated in the case of nitrous oxide and the azides[9] suggests that the N—N bond, if present in the N_2O_4 molecule, must be extremely weak. The alternative structure of the dimer proposed by Pauling involves a nitrogen oxygen bond and it has to be admitted that there is not enough evidence to rule it out. The other significant discrepancy noticed refers to tertiary butyl alcohol. The causes may be from two sources: the choice of the characteristic frequency and the value of the bond energy used in the calculation. From a study of a number of alcohols, it appears that the characteristic frequency of the C—O bond is in the neighbourhood of 1050 $cm.^{-1}$ Accurate values of the bond distance in this compound are not readily available but from single bond covalent radii of the two atoms and the bond distance-bond energy curve of Skinner,[10] the bond energy value for this bond turns out to be nearer 70,000 cals. than the value used. Using these values, the calculated value for the decomposition reaction works up to 66,000 cals. which is quite close to the experimental value of Kistiakowski[7] quoted by Fugassi and Warrick (*loc. cit.*).

Flett (*loc. cit.*) has observed that a close correlation can be noticed between Hammett's σ factor[4] and the characteristic frequency, but it has to be stated that Hammett's empirical equation is subject to certain limitations. The σ and ρ factors sometimes show variations which may amount to as much as 25% of their values (*e.g.*, *p*-methoxy and *p*-amino and *p*-methyl show variations in the σ factor while bromination of acetophenone show variations in the ρ factor). The existence of resonance in the structures compared also causes considerable deviations from the generalisations. Any relationship involving characteristic frequencies and activation energies can give values which are nearer but even this is subject to the restriction that comparisons can be made, only if the mechanism of the reaction can be considered to be the same. This has been taken note of in the present analysis, and the relationship found is just an empirical one which may with a fuller data on all the factors influencing the course of the reaction lend itself to theoretical computation.

Summary

A linear relationship is observed between the square of the bond frequency and the activation energy in the case of a few reactions in which substituents in the para-position are changed. Earlier work on similar problems is discussed and some discrepancies accounted for.

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A COLOUR REACTION OF CERTAIN PHENOLIC ETHERS AND THEIR DERIVATIVES WITH NITRIC ACID

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In the course of work on the synthesis and study of anthoxanthins and their degradation products in this laboratory a number of derivatives of phenolic ketones became available. It was noticed that some of them gave a blue colour reaction with concentrated nitric acid. It appears to be characteristic of certain structural combinations and comes in handy for distinguishing between closely related compounds and isomers belonging not only to the abovementioned group of phenolic ketones, but also to simpler (phenolic ethers) and more complex types (chalkones and flavanones) of compounds.

In order to describe the colour reaction, phloroacetophenone dimethyl ether could be taken as a typical example. When a small quantity of this substance is treated with concentrated nitric acid the solid goes into solution producing a brilliant blue colour. On standing, this colour gradually changes through an intermediate violet to a bright scarlet red which is stable. This colour change becomes more rapid when the solution is heated. The blue is not obtained with other mineral acids even when used in conjunction with nitric acid. Dilute nitric acid also fails to produce it; its solvent capacity is also very small as compared with the concentrated acid. It should be emphasised here that the appearance of a definite blue or green colour immediately or within a few minutes after the substance is treated with nitric acid can alone be taken as a positive test or reaction and not any other colour such as yellow, orange red or brown commonly given by most organic compounds. The following is a list of compounds (not exhaustive) yielding positive tests:—

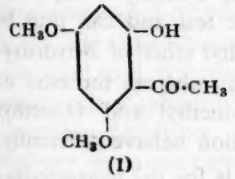
(1) *Phenolic ethers.*—Resorcinol-dimethyl and diethyl ethers and orcinol dimethyl ether give an intense emerald green colour immediately. The trimethyl ether of phloroglucinol produces a deep blue colour in about two minutes.

(2) *Aldehydes.*—Resorcylic-aldehyde-4-methyl ether gives a green colour within a minute while phloroglucin-aldehyde-4: 6-dimethyl ether gives an immediate blue colour.

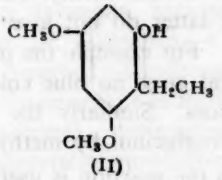
(3) *Ketones.*—4-Methyl and 4-ethyl ethers of β-resacetophenone and its dimethyl ether and γ-resacetophenone-monomethyl ether give a greenish blue colour within two minutes. Immediate pure blue colour is formed by the following:—Phloroacetophenone-4: 6-dimethyl-, diethyl-, dibenzyl-, 4-benzyl-6-methyl, and 2: 4: 6-trimethyl ethers; ω-methoxy-phloroacetophenone-4: 6-dimethyl and diethyl ethers; ω-ethoxy-phloroacetophenone-4: 6-diethyl ether, phlorobenzophenone-4: 6-dimethyl and 4: 6: 2′- trimethyl ethers and ω-phenyl-phloroacetophenone-4: 6-dimethyl ether.

(4) *Acids and their derivatives.*—β-Resorcylic acid-4-methyl ether gives a green colour in a minute; it is rather sparingly soluble. The dimethyl ether, its acid chloride and its anhydride give immediate blue colour. β-Resorcylic-ester-4-methyl and 2: 4-dimethyl ethers, everninic acid and its methyl ester and the dimethyl ether of methyl orsellinate give a similar colour.

Catechol, quinol, pyrogallol and hydroxy quinol and their methyl ethers do not give this test. Even resorcinol, orcinol and phloroglucinol and their partial methyl ethers do not give it; only their fully methylated ethers do and they represent the simplest types. It would therefore appear to be a characteristic of the fully alkylated ethers of the three meta-hydroxy-phenols. One hydroxyl could be free if it is protected by a carbonyl group in the neighbouring position. Examples of these are given above in (2), (3) and (4). This should be connected with the effect of chelation known to exist in the case of orthohydroxy-carbonyl compounds. Support for this explanation is provided by the following comparisons. Compounds (I) and (III) give positive tests whereas the related compounds (II), (IV) and (V) do not. It should be emphasised that a carbonyl group is capable of protecting only one hydroxyl group by chelation and hence phloroacetophenone-4-methyl and 4-benzyl ethers and γ-resacetophenone give negative reaction. As could be expected free phloroacetophenone and resacetophenone do not respond to the test.



(I)



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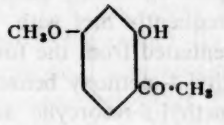

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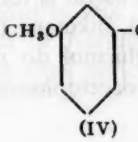

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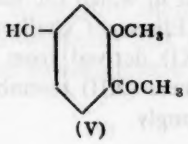


(V)

A large variation in the nature of the carbonyl group is permissible since aldehydes, ketones, including ω-alkoxy and ω-aryl ketones, acids and esters behave alike. Though protection of the hydroxyls by benzyl groups leads to positive reaction, protection by acyl groups like benzoyl gives only negative test (*e.g.*) 2: 4-dibenzoyl-phloroglucinaldehyde.

Further substitution with methyl or methoxyl groups in the nuclear positions of phloroacetophenone-2: 4-dimethyl ether or in the 3 and 5 positions of β-resorcylic acid- and β-resacetophenone-4-methyl ethers produces negative reaction. Typical examples are 2-hydroxy-3: 4- and 2-hydroxy-4: 5-dimethoxy acetophenones, 2-hydroxy-3: 4: 6, 2-hydroxy-3: 4: 5- and 2-hydroxy-4: 5: 6-trimethoxy acetophenones, 2-hydroxy- ω: 3: 5: 6-tetramethoxy acetophenone, 2-hydroxy-3-methyl-4-methoxy- and 2-hydroxy-3-methyl-4: 6-dimethoxy acetophenones, and 2-hydroxy-3-methyl-4-methoxybenzoic ester. These do not give the test.

A consideration of all the above particulars would indicate that the structural requirements for this colour reaction with nitric acid can be represented as given below:

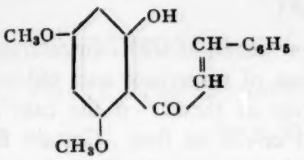
(VI) (VII)

R = H, CH_3 or OAlk.

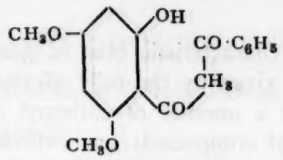
R' = H, CH_3, CH_2 aryl, C_6H_5, CH_2 OAlk., OH, OAlk.

Consequently it offers a ready means of distinction between these types and others that may be obtained by the degradation of flavones, flavonols and related compounds. Further in the methylation of derivatives of resorcinol and phloroglucinol, besides the normal methyl ethers, C-methyl compounds are frequently met with. The latter do not give the test and can thus be differentiated from the former. For example the methyl ether of 2-hydroxy-3-methyl-4-methoxy benzoic acid gives no blue colour, whereas the ester of 4-O-methyl-β-resorcylic acid does. Similarly the C-methyl and O-methyl derivatives obtained from phloroglucinol by methylation behave differently.

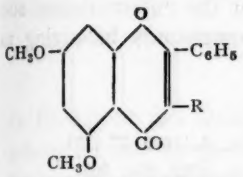
Another direction in which the reaction is useful is for the characterisation of flavanones. Ethers of chalkone (VIII), diketone (IX), flavone (X), and coumaranone (XI) derived from phloroglucinol do not give the test, whereas flavanone ethers (XII) resemble phloroacetophenone-dimethyl ether and give the test strongly.



(VIII)

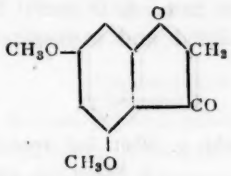


(IX)

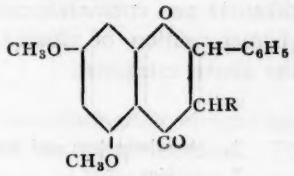


R=H or OCH_3

(X)

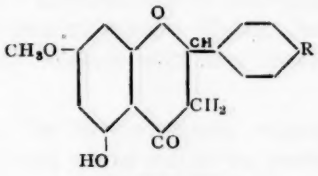


(XI)



R=H or OCH_3

(XII)



R=H, OH or OCH_3

(XIII)

The observation that a free hydroxyl in the 5-position of flavanones (XIII) is no hindrance to this test makes the characterisation of flavanones more easy, because partial methylation of hydroxy flavanones leaving this 5-hydroxyl free is readily carried out and this keeps the flavanone ring in tact.[1] On the other hand, complete methylation results in the opening of the ring and formation of chalkone derivatives. The presence of methyl ether groups and even free hydroxyl groups in the side phenyl nucleus does not seem to affect the reaction. The scope is indicated by the following list of flavanones:—5:7-dihydroxy flavanone, naringenin (5: 7: 4′-trihydroxy flavanone) and isosakuranetin (5: 7-dihydroxy-4′-methoxy flavanone) do not give the test whereas 7-methoxy-5-hydroxy flavanone, sakuranetin (7-methoxy-5: 4′-dihydroxy flavanone), sakuranetin-monomethyl ether (7: 4′-dimethoxy-5-hydroxy flavanone), naringenin-trimethyl ether (5: 7: 4′-trimethoxy flavanone) and hesperetin-trimethyl-ether (5: 7: 3′: 4′-tetramethoxy-flavanone) give positive test. In this connection should be mentioned the earlier observation of Asahina and co-workers[2] that sakuranetin gives an indigo blue colour with nitric acid and isosakuranetin does not.

Summary

A characteristic blue or green colour reaction with concentrated nitric acid is given by the fully alkylated ethers of resorcinol and phloroglucinol and by a number of carbonyl derivatives of them. n the case of these carbonyl compounds one orthohydroxyl could be free. Certain flavanone derivatives of phloroglucinol also give this test whereas chalkones, flavones, diketons and coumaranones do not. It is useful for the differentiation and characterisation of closely related and isomeric compounds belonging to the above categories.

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STUDIES IN COLLOID OPTICS

Part II. The Sol-Gel Transformation of Gelatin Gels

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Introduction

In Part I[1] of this series the sol-gel and gel-sol transformation of agar-agar gels by the new simple technique of R. S. Krishnan has been discussed. The mechanism of the gel-sol and sol-gel transformation suggested by the results in the case of agar-agar gels indicated that it would be worth while to study the sol-gel and gel-sol transformation of some more gels. In the present paper we take up the case of gelatin. Gelatin has attracted the attention of a number of earlier workers who have investigated its properties by different methods.

It is evident that the light-scattering technique of investigating the structure of gelatin sols and gels as well as the mechanism of the transformation from one state to the other is superior to any other method such as the study of the changes in viscosity, etc. The optical method has the advantage that we do not disturb the transformation taking place. Arisz[2] has studied the Tyndall effect of Glycero-sols of gelatin by using a photographic method of recording the intensity of the scattered light. He found that the intensity of the Tyndall cone depends upon (1) the temperature, (2) the previous history and (3) the concentration of gelatin, the intensity being greater the lower the temperature and the higher the concentration of the gel used. Dexter and Kraemer[3] have made a study of the effect of hydrogen-ion concentration upon the intensity of scattering of light by gelatin sols. They found a sharp rise in intensity at the isoelectric point at and below 25° C. but above 40° C. the variation in pH had no marked effect on the light scattering capacity of the sols. They made use of this observation to locate the iso-electric point in gelatin from various sources and mixtures. However, as we have seen already, the light-scattering technique of R. S. Krishnan[4] with the aid of a pair of double-image prisms and the resulting four Tyndall cones gives a more precise means of understanding the shape and the size of the colloid particles.

Recently Subbaramiah[5] studied the effect of hydrogen-ion concentration upon gelatin sols by the technique of R. S. Krishnan. He has shown that

the increase in intensity near the iso-electric point is due to the formation of aggregates by the gelatin particles as shown by the decrease in the depolarisation ρH with incident horizontally polarised light.

Krishnamurthi[6] studied the sol-gel and gel-sol transformation of gelatin by means of the then known technique of studying the intensity and the depolarisation with only one beam of unpolarised light. He indicated that even in the sol state the gelatin particles are of a size comparable to the wave-length of light but a study of the scattered light with incident unpolarised light alone does not provide sufficient data for our purpose. A study of the intensity I with unpolarised light and of ρ_v and ρ_H, the depolarisation of scattered light with incident beam polarised with its electric vector vertical and horizontal respectively, appears to be essential in order to follow the changes in the size and the shape of the colloidal gelatin particles during the transformation from the sol to the gel state and *vice versa*. Moreover, the gelation is a function of time also; though Krishnamurthi has mentioned this he does not appear to have taken it into consideration in his study, for it is possible to obtain gels at higher temperatures than those given by Krishnamurthi if only sufficient time were allowed. In the present study we have dealt with the changes in intensity and depolarisation with time at various temperatures with gelatin sols of various concentrations, *viz.*, 0·2%, 0·5%, 1·0%, 1·5%, 2·0%, 2·5% and 3·0%. The first two sols do not set to a gel and the rest give fairly good gels above 10° C.

2. Preparation of the Sols

Gelatin in the form of white sheets was powdered and washed with an acetic acid solution at pH 4·8 and then washed several times with distilled water. The powder was then allowed to dry. A weighed quantity of the powder was allowed to swell in distilled water for a day and then kept in a water-bath at 55° C. for some time until it passed into solution. The sols obtained in this manner were filtered several times so as to secure clear sols. The sols used for experiments showed no speck of dust or any other coarse particles when examined in a beam of concentrated light, only a Tyndall cone of blue light being present.

3. Measurement of the Intensity of the Scattered Light

Measurements of the intensity of the light scattered at right angles to the incident beam at various intervals as well as of the distribution of the intensity of the scattered light in various directions in the horizontal plane were made by means of the electronic photometer and the light scattered by a centimetre layer of the medium has been calculated and expressed as a fraction of the original intensity as described in the earlier paper. In the

case of high intensities the incident intensity was decreased suitably by reducing the aperture.

4. Measurement of the Depolarisation Values ρ_H, ρ_v and ρ_u

The method of obtaining the four R. S. Krishnan components by suitably placing the double-image prisms and the measurement of the depolarisation ρ_u, ρ_v and ρ_H with incident beam unpolarised, and polarised with its electric vector vertical and horizontal respectively by means of a nicol and divided circle have already been described in the earlier paper.

5. Experimental Procedure

The gelatin sol prepared as in para 2 was poured into a rectangular glass cell with plane parallel sides which was surrounded with water at 55° C. for a few minutes; the temperature was then decreased by one degree and maintained at 54° C. for several hours. Intensity and depolarisation were measured at intervals of half an hour. No change in intensity and depolarisation could be observed even after 12 hours at this temperature. The same observations were repeated successively at lower temperatures, every time starting with the sol at 55° C. to keep the previous history of the sol the same. Above 30° C. no changes in intensity and depolarisation are observed even after 12 hours. Below 30° C., however, the sol becomes viscous and more opalescent with time. The changes in intensity are measured at half-hourly intervals until they are constant; finally, the depolarisation values, *viz.*, ρ_u, ρ_v and ρ_H are also measured.

In the study of the gel-sol transformation the gels were all kept at 8° C. for 6 hours and then slowly raised to the respective temperatures and maintained at those temperatures until no further change in the intensity and depolarisation could be noticed and the final steady values of the intensity and depolarisation were recorded. The changes during the gel-sol transition in the intensity or depolarisation do not follow the reverse path of the sol-gel transformation. The gel state persists upto about 25° C. above which the gel becomes loose and gradually gets into the sol-state without showing any sharp temperature of the gel-sol transition. Above 40° C., however, gelatin remains only in the sol state.

6. Correction for the Loss in the Scattered Light when it Passes through the Layer of the Gel Intervening Between the Observer and the Incident Beam

A beam of light passing through a diffusing medium undergoes depletion by scattering. The transversely scattered light which passes through the thin layers of the medium between the observer and the scattering centre

suffers a depletion due to the rescattering by the thin intervening layer. In order to correct for this depletion the following auxiliary experiment was performed. The gel was prepared in a test-tube with one centimetre diameter and by finding the intensity distribution in the horizontal plane, the light scattered by one centimetre layer of the medium in a solid angle was calculated as usual. Using the photometer in combination with a strong filter of prussian blue it was possible to compare the total loss by scattering in one centimetre thickness of the medium with the loss in transmission (as described in the earlier paper). The values of depletion in a centimetre thickness of the medium and the loss due to scattering in the case of the gels at 10° C. are given in Table I.

TABLE I

Concentration of the gel. %	Total light scattered by 1 cm. of the layer over a solid angle 4π%	Loss in transmission per cm. %
0·2	0·6	0·6
0·5	1·5	1·7
1·0	3·3	3·3
1·5	5·1	5·0
2·0	6·4	6·6
2·5	7·6	7·8
3·0	10·2	10·4

From the above table it is clear that most of the loss of intensity during the passage of the medium is due to scattering. The layer of the medium, through which the track of the primary beam was observed in our experiment was 3 millimetres. The intensities measured by the photometer were therefore corrected for the depletion by a 3 millimetre layer, making use of the data in the last column of Table I.

Discussion of Results

(*a*) *Variation in Intensity*

(i) *Sol-gel transition*.—The variations with time of the intensity of the transversely scattered light with incident unpolarised light has been measured at different temperatures for sols of concentrations 0·2%, 0·5%, 1·0%, 1·5%, 2·0%, 2·5% and 3·0%. Figs. 1 and 2 show the data in respect of the concentrations of 0·2% and 3·0%. The variation of intensity is similar in all cases, increasing rapidly during the earlier stages and later tending to attain a saturation or a constant value. The rate of increase in intensity increases with decrease in temperature and with the increase in the concentration of sols. The curves for concentrations of 0·5%, 1·0%, 1·5%,

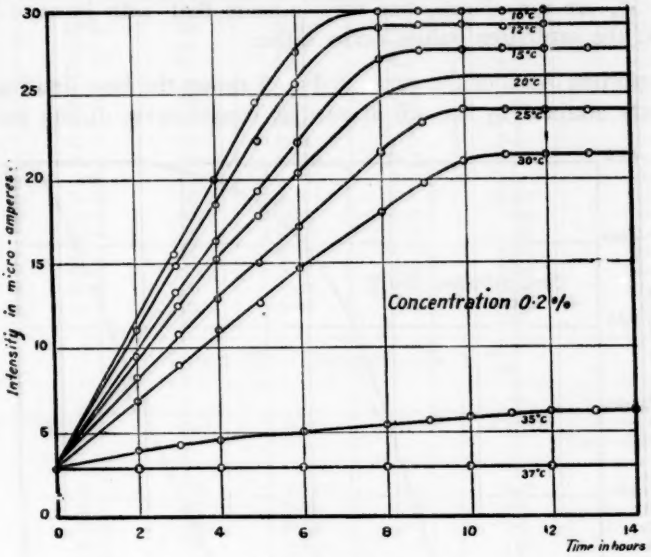
Intensity in micro-amperes.
Time in hours
Concentration 0·2 %
10°C
12°C
15°C
20°C
25°C
30°C
35°C
37°C

FIG. 1

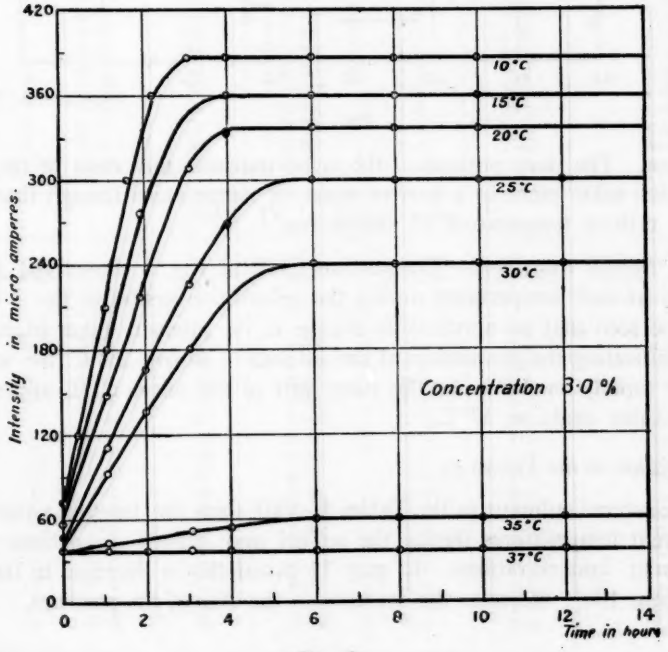
Intensity in micro-amperes.
Time in hours
Concentration 3·0 %
10°C
15°C
20°C
25°C
30°C
35°C
37°C

FIG. 2

2·0%, 2·5% are not shown, but they indicate that with increase of concentration the saturation values occur earlier.

The portion ABC of the curve in Fig. 3 shows the final limiting values of intensity attained by the sol at various temperatures during the sol-gel

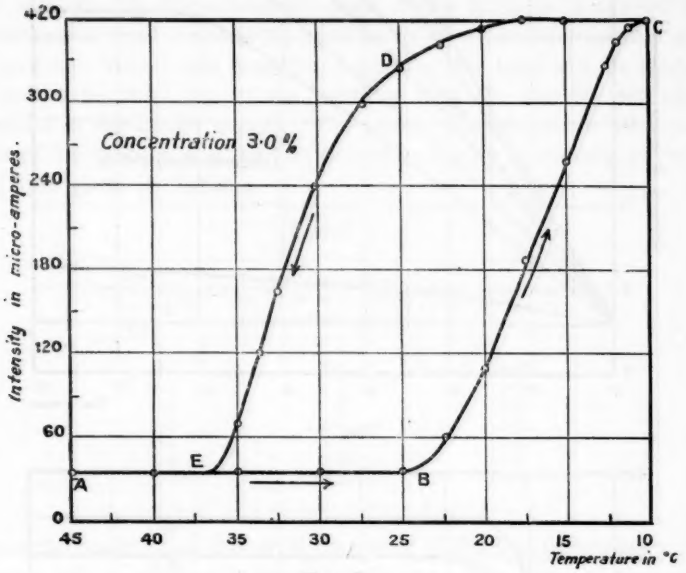

FIG. 3

transition. The steep portion of the curve indicates that most of the sol-gel conversion takes place in a narrow range of temperature though there is no definite critical temperature of conversion.

(ii) *Gel-sol transition.*—The portion CDE of Fig. 3 shows the limiting intensity at each temperature during the gel-sol conversion of the 3·0% gel. It can be seen that no appreciable change in the intensity takes place up to 25° C. indicating the persistence of the gel state. Above 25° C. the intensity falls off rapidly as shown by the steep part of the curve CDE approaching the sol value again at 37° C.

(*b*) *Variation in the Values* ρ_H

The second columns in the Tables II–VIII show the limiting values of ρ_H at different temperatures during the sol-gel and gel-sol transitions of gels of different concentrations. It may be noted that a decrease in the value of ρ_H from 100% indicates the increase in the size of the particles.

TABLE II. *Concentration* 0·2%

	Temperature in °C.	ρ_H%	ρ_0%	ρ_u% cal.	ρ_u% obs.	Total light scattered by one centimetre layer of the medium %
Sol-gel	45·0	80	0·89	2·0	2·3	0·06
	25·0	80	0·89	2·0	2·3	0·06
	22·5	75	0·83	2·0	2·1	0·10
	20·0	70	0·70	1·7	1·6	0·18
	17·5	65	0·61	1·5	1·4	0·32
	15·0	60	0·45	1·2	1·3	0·43
	12·5	55	0·34	1·0	1·2	0·54
	10·0	50	0·23	0·7	0·8	0·58
Gel-sol	8·0	50	0·17	0·5	0·6	0·60
	15·0	50	0·17	0·5	0·52	0·60
	20·0	55	0·34	1·0	1·20	0·59
	25·0	60	0·45	1·2	1·30	0·48
	30·0	70	0·70	1·7	1·80	0·42
	35·0	75	0·83	2·0	2·10	0·12
	37·0	80	0·88	2·0	2·10	0·06
	45·0	80	0·88	2·0	2·10	0·06

TABLE III. *Concentration* 0·5%

	Temperature in °C.	ρ_H%	ρ_0%	ρ_u% cal.	ρ_u% obs.	Total light scattered by one centimetre layer of the medium %
Sol-gel	45	80	0·89	2·0	2·3	0·15
	25	80	0·89	2·0	2·3	0·15
	22·5	75	0·83	2·0	2·1	0·25
	20	70	0·70	1·7	1·8	0·42
	17·5	65	0·60	1·5	1·4	0·80
	15·0	60	0·50	1·5	1·4	1·20
	12·5	55	0·35	1·2	1·2	1·20
	10·0	50	0·34	1·0	1·0	1·50
Gel-sol	8·0	45	0·32	1·0	1·0	1·50
	15·0	45	0·32	1·0	1·0	1·50
	20·0	55	0·35	1·2	1·2	1·50
	25·0	60	0·50	1·5	1·4	1·30
	30·0	65	0·60	1·5	1·4	1·70
	35·0	70	0·70	1·7	1·8	0·20
	37·0	80	0·89	2·0	1·9	0·15
	45·0	80	0·89	2·0	1·9	0·15

TABLE IV. *Concentration* 1%

	Temperature in °C.	ρ_H%	ρ_0%	ρ_u% cal.	ρ_u% obs.	Total light scattered by one centimetre layer of the medium %
Sol-gel	45·0	80	0·89	2·0	2·3	0·3
	25·0	80	0·89	2·0	2·3	0·3
	22·5	75	0·83	2·0	2·1	0·5
	20·0	65	0·61	1·5	1·7	0·85
	17·5	55	0·54	1·5	1·7	1·6
	15·0	50	0·40	1·2	1·3	2·3
	12·0	50	0·50	1·5	1·6	3·3
	10·0	40	0·61	2·0	2·1	3·3
Gel-sol	8·0	40	0·61	2·0	2·1	3·3
	15·0	40	0·61	2·0	2·3	3·3
	20·0	45	0·47	1·5	1·6	3·1
	25·0	50	0·50	1·5	1·7	2·6
	30·0	65	0·52	1·3	1·4	1·9
	35·0	70	0·61	1·5	1·5	0·5
	37·0	80	0·89	2·0	2·1	0·3
	45·0	80	0·89	2·0	2·1	0·3

TABLE V. *Concentration* 1·5%

Temperature in °C.		ρ_H%	ρ_0%	ρ_u% cal.	ρ_u% obs.	Total light scattered by one centimetre medium %
Sol-gel	45·0	80	0·89	2·0	2·3	0·50
	25·0	80	0·89	2·0	2·3	0·50
	22·5	75	0·85	2·0	2·1	0·70
	20·0	70	0·82	2·0	2·0	1·30
	17·5	60	0·75	2·0	2·0	2·20
	15·0	55	0·54	1·5	1·4	3·40
	12·5	50	0·50	1·50	1·4	5·00
	10·0	40	0·61	2·00	1·9	5·10
Gel-sol	8·0	40	0·71	2·5	2·3	5·10
	15·0	40	0·71	2·5	2·6	5·10
	20·0	45	0·64	2·0	1·9	5·10
	25·0	50	0·64	2·0	1·8	3·60
	30·0	60	0·56	1·5	1·6	3·00
	35·0	70	0·70	1·7	1·8	0·70
	37·0	80	0·89	2·0	2·1	0·50
	45·0	80	0·89	2·0	2·1	0·50

TABLE VI. *Concentration* 2·0%

Temperature in °C.		ρ_H%	ρ_0%	ρ_u% cal.	ρ_u% obs.	Total light scattered by one centimetre medium %
Sol-gel	45	80	0·89	2·0	2·3	0·60
	25	80	0·89	2·0	2·3	0·60
	22·5	75	0·86	2·0	2·1	1·00
	20·0	70	0·61	1·5	1·6	1·80
	17·5	60	0·56	1·5	1·6	3·30
	15·0	50	0·67	2·0	2·1	4·80
	12·5	40	0·71	2·5	2·4	5·40
	10·0	35	0·80	3·0	2·8	6·00
Gel-sol	8·0	35	0·80	3·0	2·8	6·40
	15·0	35	0·80	3·0	3·2	6·40
	20·0	40	0·71	2·5	2·6	6·20
	25·0	45	0·67	2·0	2·3	5·40
	30·0	50	0·55	1·5	1·6	3·80
	35·0	70	0·70	1·7	1·8	1·00
	37·0	80	0·89	2·0	2·2	0·06
	45·0	80	0·89	2·0	2·2	0·06

TABLE VII. *Concentration* 2·5%

Temperature in °C.		ρ_H%	ρ_0%	ρ_u% cal.	ρ_u% obs.	Total light scattered by one centimetre medium %
Sol-gel	45	80	0·89	2·0	2·3	0·75
	25	80	0·89	2·0	2·1	0·75
	22·5	75	1·01	2·5	2·6	1·25
	20·0	70	1·23	3·0	2·6	2·10
	17·5	60	1·31	3·5	3·3	4·00
	15·0	50	1·33	4·0	4·20	6·00
	12·5	35	1·36	5·0	4·90	6·00
	10·0	30	1·38	6·0	5·8	7·60
Gel-sol	8·0	30	1·38	6·0	5·8	7·60
	15·0	30	1·38	6·0	6·2	7·60
	20·0	35	1·36	5·0	5·1	7·40
	25·0	50	1·33	4·0	4·1	6·50
	30·0	60	1·31	3·5	3·4	3·50
	35·0	70	1·23	3·0	3·0	1·00
	37·0	80	0·89	2·0	2·2	0·75
	45·0	80	0·89	2·0	2·2	0·75

TABLE VIII. *Concentration* 3·0%

Temperature in °C.		ρ_H%	ρ_0%	ρ_u% cal.	ρ_u% obs.	Total light scattered by one centimetre medium %
Sol-gel	45	80	0·89	2·0	2·3	1·00
	25	80	0·89	2·0	2·1	1·00
	22·5	75	1·01	2·5	2·4	1·50
	20·0	70	1·23	3·0	2·8	2·50
	17·5	60	1·31	3·5	3·4	4·60
	15·0	50	1·33	4·8	4·9	7·30
	12·5	45	1·36	5·0	5·2	10·00
	10·0	35	1·38	6·0	6·1	10·20
Gel-sol	8·0	25	1·48	7·0	6·9	10·20
	15·0	25	1·48	7·0	7·2	10·20
	20·0	35	1·38	6·0	6·2	10·0
	25·0	45	1·36	5·0	5·1	7·8
	30·0	50	1·33	4·8	4·7	6·0
	35·0	70	1·23	3·0	2·9	1·5
	37·0	80	0·89	2·0	1·9	1·0
	45·0	80	0·89	2·0	1·9	1·0

(i) *Sol-gel transition.*—It may be seen that even in the sol state the size of the colloidal gelatin particles is not very small in comparison with the wavelength of light. Moreover, the values of ρ_H in the sol state do not appreciably differ with concentration indicating that the size distribution of the particles does not change appreciably in the range of concentrations investigated. During the conversion from the sol to the gel state the value of ρ_H steadily decreases till it reaches a minimum value corresponding to the particular temperature. The changes in the values of ρ_H therefore indicates that the particle size increases with time approaching limiting values. The limiting maximum value increases with the decrease in the temperature as well as with increase in the concentration.

(ii) *Gel-sol transition.*—During the gel-sol transition, however, the values of ρ_H, show that the size of the particles remains constant up to 20° C. and then falls off rapidly to the original sol values of 40° C.

It may also be noted that even when the sol becomes viscous the intensity as well as the depolarisation ρ_H do not appreciably change showing that the particle size remains constant even when viscosity has increased appreciably. Also, later on, the intensity and ρ_H change slowly with time indicating the actual growth of the particles in the gels of all concentrations. It is interesting to note that the particle size in all concentrations is roughly the same as indicated by almost a constant value of ρ_H and yet the changes in viscosity are rapid. It is therefore evident that the viscosity changes during the conversion of sol to gel occur before the particles suspended in the medium begin to swell.

(*c*) *Variations in the Values of* ρ_v

(i) *Sol-gel transition.*—The changes in the depolarisation ρ_v with decrease in temperature are similar to those observed in the sol-gel transition of agar-agar in that they occur in three different ways in different ranges of the concentrations:

(*a*) for sols of concentrations 0·2% and 0·5% ρ_v gradually decreases with temperature;

(*b*) for 1·0%, 1·5% and 2·0% sols ρv first decreases and then increases with decrease in the temperature;

(*c*) for 2·5% and 3·0% sols ρ_v gradually increases with temperatures.

This suggests that in the first case the particles tend to become more symmetrical with decrease in temperature at first but asymmetry sets in with further lowering in the temperature. At 2·5% and 3·0% solutions the increase in the asymmetry starts right from the beginning.

(ii) *Gel-sol transition.*—It may be seen from the values of ρ_v in Tables II to VIII that the changes of ρ_v during the gel-sol transition also follow in three different ways in three ranges of concentration, *viz.*:

(*a*) for 0·2% and 0·5% gels ρ_v gradually increases with temperature;

(*b*) for 1·0%, 1·5% and 2·0% gels ρ_v first decreases and later increases with increase in temperature while,

(*c*) ρ_v gradually decreases as the temperature is increased. Thus showing that in 0·2% and 0·5% gels the anisotropy increases as the gel changes to a sol.

In 1%, 1·5% and 2·0% gels the anisotropy first decreases and then increases while in the case of gels of 2·5% and 3·5% concentration the anisotropy gradually decreases with the increase in the temperature.

(*d*) *Applicability of the R. S. Krishnan Relation in the Range Investigated*

Values ρ_u observed experimentally by using incident unpolarised beam as well as those calculated by the Krishnan relation

$$\rho_u = \frac{1 + \frac{1}{\rho_H}}{1 + \frac{1}{\rho_v}}$$

have been tabulated side by side in Tables II to VIII. It is clear that they agree closely showing that the relation

$$\rho_u = \frac{1 + \frac{1}{\rho_H}}{1 + \frac{1}{\rho_v}}$$

between the three quantities ρ_u, ρ_v and ρ_H holds good in the range of concentration investigated.

8. Mechanism of the Sol-Gel and Gel-Sol Transformation in Gelatin as Suggested by the Above Results

The above mentioned variations in intensity and the three types of variations of ρ_v at the different ranges of concentrations confirm the results obtained earlier in the case of agar-agar, *viz.*, that we have to deal with two distinct phenomena. First of all we have the solute particles of small size initially but tending to increase in size rapidly with fall in temperature as one approaches the range of temperatures associated with the sol-gel transformation. This process may occur in two stages. In the first stage (*a*) the particle tends to develop a cloud of H_2O molecules which surround it without however entering into its structure. During this stage the intensity of the scattered light does not start increasing though the medium increases in viscosity. In the next stage of swelling we have also the physical swelling of the solute particles somewhat analogous to what happens in osmosis. During this second stage the intensity increases rapidly. During the stages (*a*) and (*b*) the individual particle undergoes increase in size which makes it more symmetrical as shown by the decrease in ρ_v. The latter increase in ρ_v with further fall of temperature must be associated with the aggregation or the coagulation of the swollen particles with a tendency to form increasingly unsymmetrical groups. This tendency becomes more pronounced at higher concentrations and indeed starts at the very outset as in the case of the very high concentrations 2·5% and 3·0%.

The gel-sol transition is almost a reverse process of the sol-gel transformation in which during the first stage the unsymmetrical aggregates are broken up into individual swollen particles which results in increased symmetry and later on the decrease in the size of the individual swollen particles to the size of the original sol particle is again accompanied by an increase in the anisotropy to the original sol value. There is a sort of tendency for the gel state to persist which causes the gel-sol transformation to occur at slightly higher temperatures than the sol-gel transition.

9. Separation of Density and Anisotropy Scattering and thence an Estimation of the Increase in the Volume of the Particles

The total intensity measured by the photometer is really the sum of two types of scattering: (1) the density scattering, (2) the anisotropy scattering.

Density scattering is due to the local inhomogeneities in an otherwise continuous medium and is proportional to the square of the volume of the discontinuity. The orientation scattering I_A arises from the fact that the moment induced by the incident electric vector is not in general parallel to the direction of the incident vector. Ramanathan[7] has made detailed calculation of the effect of anisotropy of the scattering particles on the intensity of the scattered light and has shown that the effect is to increase intensity of scattering to $\frac{6+6\rho_u}{6-7\rho_u}$ times the intensity of density scattering. Therefore, from the total intensity I measured at right angles to the incident beam, the density scattering I_D and the anisotropy scattering I_A were separated by using the relations

$$I_D = I \times \frac{6-7\rho_u}{6+6\rho_u} \text{ and}$$

$$I_A = I - I_D = I - I \times \frac{6-7\rho_u}{6+6\rho_u} = I \times \frac{13\rho_v}{6+6\rho_u}.$$

As has been already mentioned the density scattering is proportional to the square of the volume of the particle and thus

$$\frac{I_{D\,(Final)}}{I_{(D\,Initial)}} = \frac{V^2_{(Final)}}{V^2_{(Initial)}}$$

where V is the volume of the scattering particle. If $V_{Initial}$ is taken to be unity then the relative volume V_{Final} of the particle after swelling is given by

$$V_{Final} = \frac{\sqrt{I_{D(Final)}}}{\sqrt{I_{D(Initial)}}} \qquad (1)$$

Table IX shows the relative volume of the particles in the gels of concentration 0·2% and 0·5% only as the gradual decrease in the anisotropy shows that the individual particles are swelling at these concentrations.

However, in higher concentrations where aggregation of the particles also takes place the density scattering (observed above) is no longer proportional to the square of the volume and equation (1) can no longer be applied.

TABLE IX

Concentration %	I_D in Sol State %	I_D in Gel State %	$V_{final} = \sqrt{\frac{I_{D\ final}}{I_{D\ initial}}}$
0·2	0·056	0·56	3·12
0·5	0·13	1·4	3·15

SUMMARY

Study of the transition from sol to gel and *vice versa* by the technique of R. S. Krishnan has been extended to the case of gelatin. Intensity distribution of the light scattered by a one centimetre layer of the scattering medium in the horizontal plane with incident unpolarised light has been measured by means of an electric photometer during the various stages of the transition and hence the total light scattered in all directions by a centimetre layer of the scattering medium during the transition has been estimated as a fraction of the incident intensity. The depletion of the light transmitted through a one centimetre layer of the gel has also been measured and shown to be equal to the total light scattered by the gel. The detailed study of the variations in intensity and depolarisation during the sol-gel and gel-sol transition suggest, that

(1) there is a great similarity between the sol-gel and gel-sol transition of agar-agar and gelatin gels,

(2) the R. S. Krishnan relation,

$$\rho_u = \frac{1 + \frac{I}{\rho_H}}{1 + \frac{I}{\rho_v}}$$

holds throughout the range investigated.

(3) the transition from sol-gel is characterised by distinct stages. Firstly, the solute particle appears to develop a cloud of H_2O molecules round itself which results in an increase in viscosity without any sensible change in the light scattering capacity of the gel. The actual size then increases as indicated by the great increase in the light scattering capacity as well as the decrease in the value of ρ_H as compared with the sol,

(4) the values of ρ_v indicate that

(*a*) the particles grow more symmetrical as their size increases for concentrations up to 0·5%,

(*b*) the particles first tend towards symmetry and later grow more and more unsymmetrical with increase in size for concentrations of 2 1·0% and 1·5% and 2% while,

(*c*) the tendency for the particles to grow more unsymmetrical with increase in size exists from the very start for concentrations of 2·5% and more.

11. Acknowledgement

In conclusion, I wish to express my deep gratitude to Dr. L. A. Ramdas, Director of Agricultural Meteorology, for suggesting me the problem, for guidance and encouragement during the course of investigation and for facilities given during the work. My thanks are also due to Mr. R. S. Kale for building the photo-electric unit used in the present investigation.

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ON THE SKEWNESS OF DISTRIBUTION OF THE GENERATORS OF A RULED SURFACE

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1. In a paper published in the *Bulletin of the Calcutta Mathematical Society*, the author has proved that the line of striction of the generators of a ruled surface is also the locus of the feet of transversals intersecting consecutive and ultimately coincident generators of the ruled surface at the same constant angle. A certain measure, called the skewness of distribution of the generators has been introduced, the vanishing of which means that the generators are all parallel to the same plane. It is also proved that this measure is independent of the directrix chosen and that it is connected with the curvature properties of the surface and in particular, the skewness of distribution is equal to the sum of the product of the parameter of distribution and the first curvature at the central point and the cotangent of the angle in which the line of striction cuts the generators.

2. The object of the present paper is to examine under what circumstances the skewness—μ—is constant. It is proved that if μ be constant, the generators make a constant angle with a fixed direction. It is also proved that if the osculating quadrics of the ruled surface are equilateral hyperboloids, μ is equal to half the cotangent of the angle in which the line of striction cuts the generators. Dini-Beltrami's Theorem about ruled W-surfaces, which appears to be incomplete in its statement, is completed and it is proved that ruled W-surfaces are of two types but in both the types the relation between J and $\sqrt{-K}\,(=\tau)$ is of the form

$$aJ = \tau^{1/2} + b\tau^{3/2}.$$

The relation between the Laguerre function along a curve and the skewness of distribution of the normals to the surface along the curve is obtained.

3. Lines drawn through a point, parallel to the generators of a scroll, cut the unit sphere with the point as centre, in points which trace out a curve called the spherical indicatrix of the generators. For the spherical indicatrix, in the notation of Weatherburn's Differential Geometry, we have

$$r = d, \qquad ts' = d'$$

$$kns'^2 + ts'' = d''$$

$$\therefore \quad [r, t, n]\, ks'^3 = [d, d', d'']$$

where k is the curvature, n the principal normal of the spherical indicatrix and dashes denote differentiation w.r.t. the arc of the directrix curve. Now because, $|\, d' \,| = s'$,

$$[d, d', d'']/|\, d' \,|^3 = k\,[r, t, n].$$

Again $n \times r = t \cos \omega$, ω being the angle that the binormal makes with the radius vector and hence

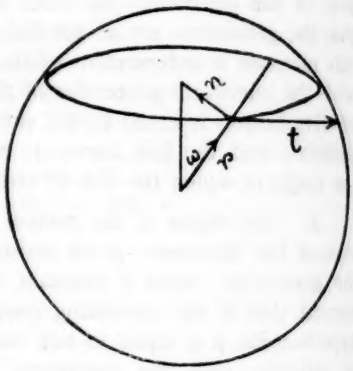
$$[n, r, t] = \cos \omega$$

and therefore, $\mu = k \cos \omega$

$$= \cot \omega \qquad (\because \quad k = 1/\sin \omega)$$

$$= \rho'\sigma/\rho,$$

where ρ and σ are the radii of curvature and torsion of the spherical indicatrix and dashes denote differentiation w.r.t. the arc. Again, because the curve is spherical,



$$\rho/\sigma + \frac{d}{ds}(\rho'\sigma) = 0,$$

i.e.,

$$\rho'/\mu + \frac{d}{ds}(\mu\rho) = 0,$$

or

$$\rho'(\mu + 1/\mu) + \mu'\rho = 0.$$

If now, μ be constant, $\rho' = 0$ and therefore ρ is constant and hence $\tau = 0$ or the spherical indicatrix is a circle and the generators are inclined at a constant angle to a fixed line—the normal to the plane of the circle. Hence we have the theorem—*The skewness of distribution is equal to the cotangent of the angle which the binormal of the spherical indicatrix makes with the radius vector and if the skewness be constant, the generators are inclined at a constant angle to a fixed line.*

4. If t be the unit tangent to the line of striction we have $t \cdot d' = 0$ and $d \cdot d' = 0$. Also if μ be const., $a \cdot d = $ const. and therefore $a \cdot d' = 0$ and hence $[a, t, d] = 0$ or the vector a lies in the plane of t and d. Hence to draw a surface with a given line of striction and skewness we draw a set of parallel straight lines at points of the given curve and in the tangent plane to the cylinder so drawn, we draw a set of lines making a constant angle with the generators. Thus there are ∞^2 of ruled surfaces with a given line of striction and skewness of distribution.

In terms of t, n, b of the line of striction, let

$$a = t \cos \theta - n \sin \theta \sin \omega + b \sin \theta \cos \omega.$$

Now because a is a constant vector, $a' = 0$ and therefore

$$\frac{d\theta}{ds} = k \sin \omega \qquad \text{(unless } \theta = 0\text{)} \tag{4. 1}$$

and

$$\frac{d\omega}{ds} + \tau = k \cos \omega \cot \theta \tag{4. 2}$$

unless $\omega = \pi/2$ when the line of striction is an asymptotic line. The first equation gives the geodesic curvature and the second, the geodesic torsion of the line of striction which will be a geodesic if θ be constant and then $\omega = 0$ (or $k = 0$) and the line of striction is a helix. Hence we have the

THEOREM.—*If the line of striction of the generators of a ruled surface whose skewness is constant be a geodesic, it must be a helix (or a straight line).*

If $\theta = 0$, the line of striction is a straight line and the generators make a constant angle with the given line as in oblique or right helicoid. If $\omega = \pi/2$, we have from the constancy of a, $\tau \sin \theta = 0$. Therefore either the curve is a plane curve when the surface is a plane or $\theta = 0$ when the line of striction is a straight line. Eliminating ds between the two equations and integrating we have

$$\sin \theta \cos \omega = c - \int \frac{\tau}{k} \sin \theta \, d\theta.$$

5. Taking the generators and their orthogonal trajectories as $v = \text{const.}$ and $u = \text{const.}$ and in the notation of Weatherburn's *Differential Geometry*, Vol. II, we have

$$\psi^2 = (u - \alpha)^2 + \beta^2,$$

$$\mathrm{J} = \frac{1}{\psi}\left[\nu - \frac{\beta'(u - \alpha) + \alpha'\beta}{\psi^2}\right],$$

and

$$\mathrm{K} = -\beta^2/\psi^4.$$

The line of striction is given by $u = \alpha$ which cuts the generators at an angle ϕ given by $\cot \phi = \pm \alpha'/\beta$. Now the value of J at the central point is given by

$$\mathrm{J}_0 = \frac{1}{\beta}[\nu - \alpha'\beta/\beta^2] = \frac{1}{\beta}[\nu - \cot \phi]$$

and therefore $\nu = \mu =$ the skewness of distribution. This gives the geometrical interpretation of ν involved in J. From the equation $\mathrm{J}_1\mathrm{K}_2 - \mathrm{J}_2\mathrm{K}_1 = 0$ which must reduce to an identity we have

$$\mu = \text{const.}, \ \beta = \text{const. and } \alpha' = \text{const.}$$

From the constancy of α' and β we have Dini-Beltrami's Theorem for a ruled W-surface.

Now because $\mu = \text{const.}$, the generators make a constant angle with a fixed vector a and therefore

$$\frac{d\theta}{ds} = k \sin \omega = 0. \qquad (\because \quad \phi = \cot^{-1} \alpha'/\beta = \text{const.}).$$

Hence either $k = 0$, *i.e.*, the line of striction is a straight line or $\omega = 0$. From the equation (4. 2) we have because θ is const.

$$\tau/k = \cot \theta,$$

and therefore the line of striction is a helix. Again because in the notation of the previous section, the value of β is given by

$$\beta = \frac{\sin (\theta - \alpha) \sin \theta}{k \sin \alpha \cos \omega} = \frac{\sin (\theta - \alpha) \sin \theta}{k \sin \alpha},$$

we have $k = \text{const.}$ because β is so and therefore τ is also constant and the line of striction is a right circular helix, the generators being drawn in the tangent planes of the cylinder making a constant angle with the generators of the cylinder.

If $k = 0$, we may take

$$r = [0, 0, f(\theta)] \text{ and } d = (\sin \alpha \cos \theta, \sin \alpha \sin \theta, \cos \alpha)$$

and because β is constant, $f(\theta) = c\theta$ and in that case the surface is a helicoid of angle α given by

$$r = (u \cos \alpha \cos \theta, u \sin \alpha \sin \theta, c\theta + u \cos \alpha).$$

If the line of striction is a right circular helix, the equation of the surface can be written as

$$\mathbf{R} = r + ud$$

where $$r = (a \cos \theta, a \sin \theta, a\theta \cot \alpha)$$

and $$d = (-\sin \theta \sin \beta, \cos \theta \sin \beta, \cos \beta).$$

When $a \to 0$, *i.e.*, the right circular cylinder shrinks to a straight line, and $\alpha \to 0$ such that $a \cot \alpha \to c$, the surface tends to

$$\mathbf{R} = (-u \sin \theta \sin \beta, u \cos \theta \sin \beta, c\theta + u \cos \beta)$$

which is a helicoid of angle β. Hence we have the

THEOREM.—*If a ruled surface is also a W-surface, the line of striction is a right circular helix (or a straight line) and the generators are lines in the tangent planes, making a constant angle with the generators of the cylinder (or a helicoid of angle α).*

6. The fundamental magnitudes of the first and second orders for the oblique helicoid

$$r = (u \sin \alpha \cos \theta,\ u \sin \alpha \sin \theta,\ c\theta + u \cos \alpha)$$

are given by $\mathrm{E} = 1,\ \mathrm{F} = c \cos \alpha,\ \mathrm{G} = c^2 + u^2 \sin^2 \alpha$

and $\mathrm{HL} = 0,\ \mathrm{HM} = -c \sin^2 \alpha,\ \mathrm{HN} = u^2 \sin^2 \alpha \cos \alpha.$

Hence $\mathrm{J} = (u^2 - 2c^2) \cot \alpha/(u^2 + c^2)^{3/2}$

and $\mathrm{K} = -c^2/(u^2 + c^2)^2$

and therefore $\tau = \sqrt{-\mathrm{K}} = c/(u^2 + c^2).$

Hence for the oblique helicoid, the functional relation is given by

$$\mathrm{J}c^{1/2} \tan \alpha = \tau^{1/2} - 3c\tau^{3/2}.$$

For the surface $\mathrm{R} = r + ud$ when the line of striction is the right circular helix $r = (a \cos \theta,\ a \sin \theta,\ a\theta \cot \alpha)$

and $d = (-\sin \theta \sin \beta,\ \cos \theta \sin \beta,\ \cos \beta)$ we have

$$\mathrm{E} = 1,\ \mathrm{F} = a \cos (\alpha - \beta)/\sin \alpha,\ \mathrm{G} = a^2 \cos e_{/}c^2\alpha + u^2 \sin^2\beta$$

$$\mathrm{HL} = 0,\ \mathrm{HM} = a \sin (\alpha - \beta) \sin \beta/\sin^2 \alpha,\ \mathrm{HN} = a^2 \sin^2 (\alpha - \beta)/\sin \alpha + u^2 \sin^2 \alpha \cos \beta$$

whence $\mathrm{K} = \dfrac{c^2}{(u^2 + c^2)^2}$ where $c = a \sin (\alpha - \beta)/\sin \alpha \sin \beta$

and $\mathrm{J} = \cot \beta\,(u^2 - bc)/(u^2 + c^2)^{3/2}$

and therefore

$$\mathrm{J}c^{1/2} \tan \beta = \tau^{1/2} - (b + c)\,\tau^{3/2}.$$

We have thus the

THEOREM—*The relation between the first and second curvatures of a ruled W-surface is of the form*

$$a\mathrm{J} = \tau^{1/2} + b\tau^{3/2}.$$

7. The osculating quadric of a ruled surface is generated by the tangents to the curved asymptotic lines, at points of a given generator. These are perpendicular to the generator at points where $\mathrm{J} = 0$ and if they are mutually perpendicular to one another, the values of u corresponding to $\mathrm{J} = 0$ must belong to the involution formed by pairs of points on the generator the tangent planes at which are perpendicular to one another, *i.e.*, $\psi = 0$.

Hence $$\mu (u - \alpha)^2 - \beta' (u - \alpha) + (\mu\beta^2 - \alpha'\beta) = 0$$

must be harmonic with

$$(u - \alpha)^2 + \beta^2 = 0$$

i.e., $2\mu - \alpha'/\beta = 0$

or $2\mu \mp \cot\theta = 0 \qquad (\because\ \alpha'/\beta = \pm \cot\theta).$

Hence we have the

THEOREM.—*If the osculating quadric of a ruled surface be equilateral, the skewness of distribution is half the cotangent of the angle in which the line of striction cuts the generator.*

8. Dr. Ram Behari has given the geometrical interpretation of the vanishing of the Laguerre function along a curve drawn on a surface, *viz.*, that the ruled surface generated by the normals to the surface has equilateral osculating quadrics. A new proof is given below in which it is also shown that the value of the Laguerre function (L) along a curve is given by

$$\mathrm{L} + \tau(2\mu + \cot\phi)/\sqrt{\tau^2 + k^2} = 0.$$

Taking the curve as $v = \text{const.}$ with unit tangent a, we have in the notation of Weatherburn's *Differeniial Geometry*

$$d = \bar{n},\ d' = a.\nabla\bar{n} = -k_n a - \tau b$$

$$d \times d' = -k_n b + \tau a$$

$$\therefore\ \beta = [t\ d'd]/|\ d'|^2 = -\tau/(\tau^2 + k_n^2).$$

$$d'' = -k_n\, a.\nabla\ a - \tau a.\nabla b - a k_n' - b\tau'$$

$$= -k_n(k_n\bar{n} + \gamma b) - \tau(\tau\bar{n} - \gamma a) - a k_n' - b\tau'.$$

$$= -(k_n^2 + \tau^2)\, n + (\tau\gamma - k_n')\, a - (k_n\gamma + \tau')\, b.$$

$$[dd'd''] = \{\gamma(k_n^2 + \tau^2) + k_n\tau' - \tau k_n'\}$$

$$\therefore\ \mu = \{\gamma(k_n^2 + \tau^2) + k_n\tau' - \tau k_n'\}/(\tau^2 + k_n^2)^{3/2}.$$

Again, the line of striction is given by

$$u(\tau^2 + k_n^2) + a.\bar{n}' = 0$$

i.e., $$u = k_n/(\tau^2 + k_n^2).$$

If T denotes the unit tangent to the line of striction

$$\mathrm{TS}' = a + ua.\nabla\bar{n} + \bar{n}\frac{d}{ds}(k_n/\tau^2 + k_n^2)$$

$$= a\frac{\tau^2}{\tau^2 + k_n^2} - \frac{k_n\tau}{\tau^2 + k_n^2}\, b + \bar{n}\frac{d}{ds}\left(\frac{k_n}{\tau^2 + k_n^2}\right),$$

$$\therefore\ \mathrm{S}'\cos\phi = \frac{d}{ds}(k_n/\tau^2 + k_n^2)$$

$$\therefore\ \cot\phi = \frac{(\tau^2 + k_n^2)^{1/2}}{\tau}\frac{d}{ds}\left(\frac{k_n}{\tau^2 + k_n^2}\right). \qquad (\tau \neq 0)$$

Hence because β is negative,

$$2\mu + \cot\phi = (2\gamma\tau - k_n')/\tau\sqrt{\tau^2 + k_n^2}$$
$$= -\mathrm{L}/\tau\sqrt{\tau^2 + k_n^2}$$

or $$\frac{\tau}{\sqrt{\tau^2 + k_n^2}}\{2\mu + \cot\phi\} + \mathrm{L} = 0.$$

Hence if $\mathrm{L} = 0$, μ and $\frac{\pi}{2} - \phi$ are both zero or constants. We have the

THEOREM.—*If a curve on a surface is a Laguerre line and if the normals along the curve make a constant angle with a given line, the line of striction of the normals cut them at a constant angle and conversely.*

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